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Research Article

Acidic Deep Eutectic Solvent as a Catalyst for the Esterification of Levulinic Acid to Ethyl Levulinate

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Abstract

Deep eutectic solvents (DESs) are environmentally friendly compounds that can be synthesized through the combination of hydrogen-bond donors and acceptors. The diverse applications of DESs underscore their potential as catalysts in various chemical reactions. In this study, an acidic DES was prepared as a catalyst for levulinic acid (LA) esterification with ethanol to produce ethyl levulinate (EL). The acidic DES was prepared from choline chloride and sulfanilic acid through thermal mixing. Characterization of the DES was conducted using Fourier transform infrared-attenuated total reflectance and nuclear magnetic resonance spectroscopy analysis to identify its functional groups and confirm the structure. Additionally, the thermal stability of the DES was analyzed using thermogravimetric analysis, while its acidity was determined using acid-base titration. The esterification of LA with ethanol was assessed under reflux conditions at 80 °C, with specific parameters examined: the molar ratio of LA to ethanol (ranging from 1:5 to 1:13), the ratio of LA to DES (ranging from 1:0.4 to 1:1.4), and the reaction duration (0.5–5 h). The DES used in this work showed an acidity of 2.89 mmol/g. The optimum conditions were obtained at a 1:7 molar ratio of LA to ethanol, a 1:1.2 ratio of LA to DES, and 3 h of reaction time at 80 °C, resulting in 99% conversion of LA to EL. This finding highlights the remarkable catalytic performance of the choline chloride/sulfanilic acid DES in facilitating a highly efficient conversion of LA to EL.

Keywords: Deep eutectic solvent; Ethyl levulinate; Esterification; Levulinic acid; Sulfanilic acid

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1. Introduction

Renewable resources are currently used to synthesize valuable chemicals, and this approach must be taken seriously due to the high demand for such products and the alarming rate of depletion of non-renewable resources. Recently, biomass has garnered considerable attention as an alternative feedstock for the production of various bio-based products [1]. Levulinic acid (LA) is a platform biomass-derived chemical that has the potential to serve as a precursor for the synthesis of numerous useful compounds. The presence of ketone and carboxylic acid functional groups is crucial in LA conversion, such as the synthesis of levulinate ester, γ-valerolactone, acrylic acid, 1,4-pentanediol, α-angelica lactone, and δ-amino levulinic acid [2]. These transformations are pivotal in fostering a more sustainable landscape within the chemical industry.

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Levulinate ester, particularly ethyl levulinate (EL), is a chemical that can be derived from biomass components and employed in a wide range of applications, including as a fuel additive. Due to its high miscibility, EL demonstrates compatibility with energy-dense fuels, such as biodiesel-diesel blends. The addition of EL into fuel blends improves various properties, including lubricity, flash point, and viscosity, as well as improving the emission profile [3]. Ethyl levulinate presents a significant advantage as a replacement for non-renewable-based fuel additives when utilizing biodiesel as a liquid fuel in diesel engines. The synthesis of EL can be achieved through the catalytic esterification of LA under moderate reaction conditions. High yields of EL have been obtained in reactions using conventional homogeneous acid catalysts, namely sulfuric acid and phosphoric acid [4]. These catalysts are homogeneously distributed in the reaction medium due to their phase compatibility, thereby eliminating mass transfer limitations between the reactants and the catalyst. The enhanced reaction kinetics facilitated by these catalysts result in high product selectivity. Although the synthesis of EL using mineral acids has proven effective, the drawbacks of equipment corrosion, environmental pollution, and challenges related to solvent recycling have contributed to a less favorable perception of these catalytic techniques [5]. Conversely, various eco-friendly heterogeneous acid catalysts have been developed for LA esterification. Nonetheless, the reduction in catalyst performance due to deactivation or poisoning, as well as the loss of active sites, has limited the utilization of solid acid catalyst reactions [6].

Ionic liquids (ILs) are organic salts with melting points below 100 °C, consisting of organic cations and either inorganic or organic anions, which exhibit properties similar to molecular organic liquids [7]. Ionic liquids serve as catalysts and alternative solvents for various biomass conversion processes. The use of ILs in catalysis is regarded as more environmentally friendly than conventional mineral acids. Ionic liquids can be reused for reactions, thereby reducing the amount of waste generated [8]. They are recognized as promising and unique liquid catalysts for LA esterification. Among the various types of ILs, deep eutectic solvents (DESs) represent a new catalysis approach that combines the benefits of both homogeneous and heterogeneous acid catalysts. A DES is made up of a hydrogen-bond donor (HDB) and a hydrogen-bond acceptor (HBA) connected by a hydrogen bond [9]. It is a low eutectic mixture that shares similar physicochemical properties with ILs. Ionic liquids are noted for their chemical stability, low vapor pressure, high dissolution, non-flammability, and low melting points. In contrast, DESs offer advantages, such as cost-effectiveness, low toxicity, and biodegradability, compared to ILs [10]. Numerous bio-based processes have employed DESs as catalysts and solvents in biomass transformation, including raw biomass [11], fructose [12], and cellulose [13]. Previous research conducted by Hu et al. [9] demonstrated that the conversion of furfuryl alcohol to EL using DES as a catalyst resulted in significantly higher selectivity for EL when DES acted as the acid catalyst. The exceptional performance in achieving high conversion of LA to EL using chorine chloride/para-toluenesulfonic acid (ChCl/pTSA) DES has been reported previously [6]. However, the catalytic role of DES in the conversion of LA to EL, as well as the impact of DES on the reaction, remains an area that has not been extensively explored.

In this study, a DES was prepared as a homogeneous catalyst for LA esterification by mixing ChCl ??? and sulfanilic acid. This DES has not been reported previously as an acid catalyst for esterification reactions. Typically, the use of homogeneous acids as catalysts requires subsequent separation or removal through the neutralization process. However, the DES synthesized using sulfanilic acid through simple mixing with ChCl facilitates the separation of the DES. This work aims to study the characteristics of DES as an acid catalyst and to evaluate its performance in the esterification of LA to EL. Characterization of the DES was performed using Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and acid-base titration to determine the presence of related functional groups, chemical structure, thermal stability, and acidity, respectively. Additionally, the effect of various reaction parameters on the esterification of LA to EL, such as the molar ratio of LA to ethanol, DES loading (LA:DES), and reaction time, was investigated.

2. Materials and Methods

2.1 Materials

Levulinic acid ($C_5H_8O_3$, 98%, Merck) and ethanol (C_2H_6O, 95%, Vchem) were acquired as reactants for EL synthesis. An acidic DES was synthesized using choline chloride ($[(CH_3)_3NCH_2CH_2OH]^+Cl^-$, 99%, Acros) and sulfanilic acid ($C_6H_7NO_3S$, 99%, Sigma-Aldrich Co.). Sodium hydroxide (NaOH, reagent grade, Vchem) and phenolphthalein (1%, Bendosen) were obtained for the titration of acids. All chemicals received from suppliers were directly used for experimental work without further purification.

2.2. Synthesis of DES

The DES was prepared by mixing ChCl as the HBA and sulfanilic acid as the HBD in a molar

ratio of ChCl to sulfanilic acid of 2:1. The method followed the previously reported synthesis method [14]. The reaction was conducted at a temperature of 140 °C for 8 h to obtain a homogeneous mixture. Then, the prepared ChCl/sulfanilic acid DES was stored in a glass tube with an airtight tube cover and placed in a desiccator.

2.3. Characterization of DES

The Fourier transform infrared-attenuated total reflectance spectroscopy (Spectrum One spectrometer) by PerkinElmer was used to analyze the chemical functional groups related to the DES structure. The analysis was performed in the IR region of 500–4000 cm^{-1}. In NMR analysis, the DES was dissolved in deuterium oxide prior to performing the ^{1}H and ^{13}C-NMR analyses using a Bruker 400 Ultrashield NMR spectrometer. The thermal degradation and stability of the DES were assessed by preparing a 10 mg sample under inert heating conditions using a Mettler-Toledo thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) 1 STAR system at a ramping temperature of 20 °C/min from 30 to 950 °C. The DES sample was heated for 10 min at 120 °C prior to the analysis. The acid-base titration method was carried out to determine the acidity of the DES. The titration was conducted using a NaOH solution prepared at a concentration of 0.01 mol/L. A sample of 0.2 g DES was diluted in 5 mL of ethanol, and then, two drops of phenolphthalein were added as a visual indicator. The mixture was mixed until the catalyst dissolved in the ethanol prior to conducting the titration. The acidity of the DES was calculated using the following Eq. 1.

$$\text{DES acidity (mmol/g)} = (V_{NaOH} \times C_{NaOH})/M_{DES} \quad (1)$$

Where, V_{NaOH} is the volume of NaOH for titration (L), C_{NaOH} is the concentration of NaOH (mmol/L), and M_{DES} is the mass of the DES (g).

2.4 Parametric Study for the Esterification of LA to EL

The esterification of LA with ethanol, as represented in Eq. 2, was conducted in a batch flask reactor under reflux conditions. Ethanol, LA, and DES were charged into the reactor, and the experiment was conducted at a fixed temperature of 80 °C, which corresponds to the reflux temperature of ethanol under the specified experimental conditions. This study investigated the effect of various parameters, including molar ratios of LA to ethanol from 1:5 to 1:13, LA to DES (LA:DES) ratios from 1:0.4 to 1:1.4, and reaction times from 0.5 to 5 h. The reaction performance of the ChCl/sulfanilic acid DES was evaluated based on the conversion of LA. The selected sample produced at optimized reaction conditions was further quantified using gas chromatography-mass spectrometry (GC-MS) for data comparability. The optimum molar ratio of LA to ethanol, LA:DES ratio, and reaction time were determined to achieve high LA conversion to EL.

$$C_5H_8O_3 \text{ (LA)} + C_2H_6O \text{ (ethanol)} \leftrightarrow C_7H_{12}O_3 \text{ (EL)} + H_2O \text{ (water)} \quad (2)$$

2.5 Analysis of LA Conversion and EL Synthesis

Acid-base titration was used to determine the moles of LA in the product mixture and calculate the conversion of LA. A NaOH solution of 0.01 mol/L was prepared by dissolving NaOH in distilled water. Each product sample, with a volume of 0.2 mL, was subjected to titration following the reaction. The sample taken was diluted in a beaker with 5 mL of distilled water, and two drops of phenolphthalein were used as a visual indicator. The moles of initial LA in ethanol were also analyzed through titration to ascertain the amount of LA present as a reactant, which was necessary for the calculations related to LA conversion. The DES sample before the reaction was titrated using the aforementioned method to determine the moles of the DES used. Subsequently, the calculation for LA conversion was performed using Eqs. 3–5 as follows.

$$\text{Moles of LA + DES in the final product} = (V_{NaOH} \times C_{NaOH} \times V_{Prod})/V_{Sample} \quad (3)$$

$$\text{Moles of LA in the final product} = (\text{Moles of LA + DES}) - (\text{Moles of DES}) \quad (4)$$

$$\text{LA conversion (\%)} = (LA_{initial} - LA_{final})/LA_{initial} \times 100\% \quad (5)$$

where, V_{NaOH} is the volume of NaOH for titration (L), C_{NaOH} is the concentration of NaOH (mol/L), V_{Prod} is the volume of the product mixture, V_{Sample} is the volume of the sample used for titration (L), LA_{final} is the moles of LA in the final product (mol), and $LA_{initial}$ is the moles of initial LA used in the reaction (mol).

Gas chromatography-mass spectrometry was used to quantify the synthesized liquid product of the selected sample using a Varian 450 GC equipped with a HP-5MS column. Standard chemicals of EL and LA were utilized to plot the calibration curves (GC-MS area vs. standard chemical concentration) and to calculate the LA conversion (%) and the EL yield (mol%) using Eqs. (5) and (6), respectively. The GC-MS oven conditions were set from 40 to 120 °C (3.0 °C/min) and 120 to 280 °C (50.0 °C/min), with the cooling temperature set at 50 °C.

$$\text{EL yield (mol\%)} = \frac{\text{Moles of EL, final}}{\text{Moles of LA, initial}} \times 100\% \quad (6)$$

3. Results and Discussion

3.1 Characterization of DES

The chemical structure of the DES was analyzed to identify related functional groups in its structure. The results of the FTIR spectrum are presented in Figure 1. The stretching vibration of N-H was observed in the range of 3300–3500 cm^{-1}, which corresponds to the N-H bonding present in the structure of sulfanilic acid [14]. A peak associated with C-H was detected between 2850 and 3000 cm^{-1}. The C=C stretching of the aromatic structure was observed between 1500 and 1700 cm^{-1}. As reported previously, the C=C stretching was detected around 1600–1750 cm^{-1} [15].

A prominent peak of S=O of the sulfonate group in sulfanilic acid was identified around 1350–1500 cm^{-1}. Furthermore, a strong C-N peak of the aromatic amine was observed at approximately 1100–1250 cm^{-1}. Conversely, a C-O peak was detected between 1000 and 1200 cm^{-1}, which may be attributed to the C-O bond in the ChCl structure and potentially indicates a chemical bonding formation between sulfanilic acid and ChCl, as both compounds can undergo esterification during the reaction. Previous research on various DES preparations has shown that C-N and C-O stretching are represented by peaks at wavenumbers between 1300 and 1000 cm^{-1} [16]. The peak detected in the range of 900–1000 cm^{-1} can be assigned to C-C stretching vibration. This peak has also been reported in the DES structure of ChCl/glucose detected from the FTIR analysis [16].

The NMR spectra demonstrate the signals corresponding to the hydrogen and carbon atoms of the ChCl/sulfanilic acid DES, as determined by their chemical shift (δ ppm) values, which are illustrated in Figures 2(a–b). The analysis is crucial for providing insights into the molecular structure of the DES and the interactions between ChCl and sulfanilic acid within the mixture.

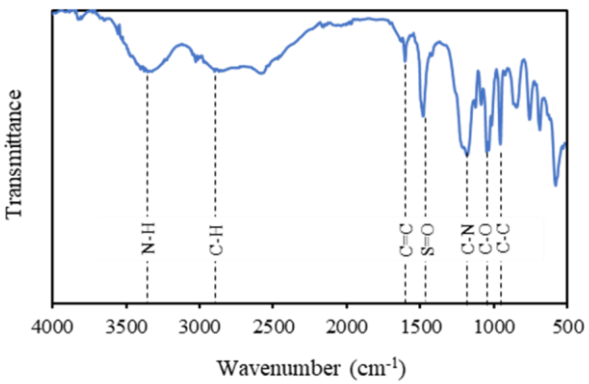

Figure 1. Fourier transform infrared spectrum of the ChCl/sulfanilic acid DES prepared in this study

Figure 2(c) displays the labeled associated functional groups in the molecular structures of sulfanilic acid and ChCl for facilitating the interpretation of the NMR peaks observed during the analysis. In the ^{1}H-NMR spectrum, the peaks observed in the range of 7.30–8.00 ppm are attributed to the aromatic protons of sulfanilic acid. The multiplet signal within this region is likely related to the presence of various carbons in the benzene ring, which exhibit different chemical characteristics due to the substitution of the –SO_3H and –NH_2 groups [17]. The singlet signal at 4.87 ppm corresponds to the proton of the –OH group [18]. The presence of this sharp peak suggests that the –OH group of ChCl is involved in hydrogen bonding interactions within the DES. Multiple peaks observed between 4.00–4.10 and 3.50–3.55 ppm are associated with the methylene groups. These observed multiple signals are proposed to arise from the interaction between the protons of these groups and the neighboring –OH group and N^+, which may influence their electron density environment. Consistent with the findings of Othman *et al.* [19], the peak at 3.20 ppm in the NMR spectrum is attributed to the protons of the quaternary ammonium (–$N(CH_3)_3$) group in the ChCl structure. The singlet nature of this peak indicates a symmetrical environment for the three methyl groups attached to the nitrogen atom, which remains in the ChCl molecule and is consistent with its known structure.

The characteristics of the ChCl/sulfanilic acid DES as observed in the ^{13}C-NMR spectrum exhibit several distinct peaks indicative of an aromatic structure. The aromatic protons are typically detected between 120.0 and 135.0 ppm, which correspond to the sulfanilic acid structure. Similar to the observations made in the ^{1}H-NMR spectrum, the presence of electron-withdrawing groups (–SO_3H and –NH_2) on the directly bonded carbon atoms within the benzene ring results in deshielding effects, thereby explaining the downfield chemical shifts and the multiple signals that verify the sulfanilic acid component in its aromatic form. A chemical shift observed at approximately 70.3 ppm is characteristic of carbon-oxygen bonds in a non-aromatic structure, such as the alcohol group [20]. This signal may correspond to the methylene carbon attached to the hydroxyl group (–CH_2OH) present in the ChCl. The prominent peaks observed in the range of 56.5–58.5 ppm are attributed to the carbon atom bonded to the nitrogen of the quaternary ammonium group of ChCl [21]. The strong signal is indicative of a relatively uniform and symmetrical carbon environment in the DES structure. The overall NMR spectra are consistent with the expected DES structure, thereby confirming the successful preparation of the eutectic mixture for catalytic applications.

Thermal stability is a critical study, which basically refers to the potential of a substance or material to withstand chemical or physical changes when exposed to extreme temperatures. The ability of a material to withstand heat treatment without experiencing structural changes or degradation is known as its thermal stability [22]. The thermal stability and degradation of the ChCl/sulfanilic acid DES catalyst are shown in Figure 3 through differential thermal gravimetric analysis (TGA-DTG) curves. The first weight loss was observed below the temperature of 150 °C. The small loss of weight is typically attributed to moisture in the sample. A significant degradation of the DES was observed in the temperature range of 200–350 °C, correlating to the degradation of ChCl and sulfanilic acid in the DES structure, and the remaining substances decomposed slowly beyond this temperature range. The curves revealed a sharp exothermic peak at approximately 240 and 287 °C, with continuous degradation up to 306.12 °C. A major weight loss occurred at this peak, with 74.69% of the sample decomposed. The majority of DES degradation occurs in the region of 190–280 °C [23]. The presence of a broader peak may suggest a multi-step degradation process, followed by a secondary reaction or a phase transition. The significant residue observed may indicate that a considerable portion of the sample did not react or decompose within this temperature range. The thermogram further illustrates the slow

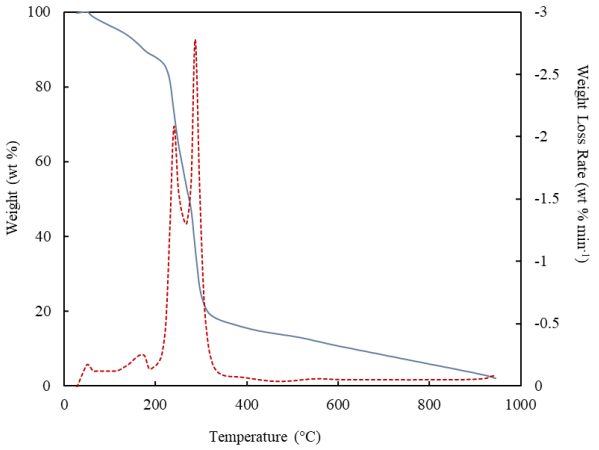

Figure 3. TGA-DTG curves of the ChCl/sulfanilic acid DES

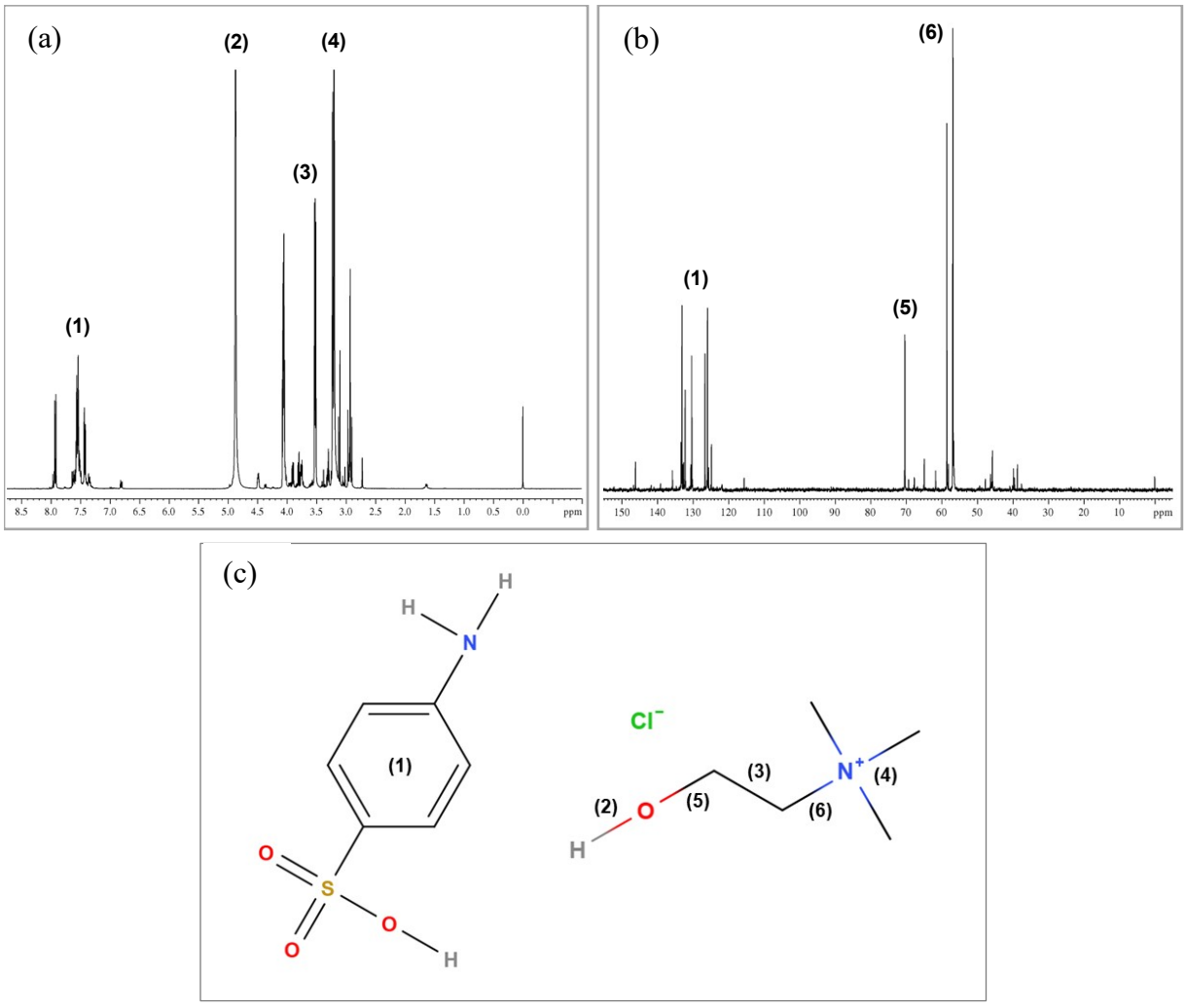

Figure 2. The peak fitting results of (a) ^{1}H and (b) ^{13}C NMR spectra, and (c) the associated functional groups in the structures of ChCl/sulfanilic acid DES

degradation of the remaining sample at 500–950 °C, with a weight loss of 11.23%. The coordinating nature of the ions in the mixtures, along with their intermolecular interactions, may contribute to elevated thermal breakdown temperatures [24]. It is advisable to conduct the synthesis of DES as catalysts at temperatures below 200 °C to ensure the thermal stability and catalytic efficacy of the catalyst.

The ChCl/sulfanilic acid DES was used as an acid catalyst to catalyze the esterification of LA to EL. The characteristics of the catalyst are important for the efficiency of this reaction. An acid catalyst is required for the esterification of LA to EL [3]. The ChCl/sulfanilic acid DES, prepared from the precursors of ChCl and sulfanilic acid—both of which are weak acids—exhibits acidic properties conducive to catalyzing the reaction. The synthesized ChCl/sulfanilic acid DES has an acidity of 2.89 mmol/g.

3.2 Reaction Mechanism of DES Synthesis

The interaction between sulfanilic acid and ChCl within the acidic DES is essential for understanding the effect on the properties of the resulting mixture, as well as its catalytic behavior in LA esterification. The combination of sulfanilic acid and ChCl does not yield a new compound because the process relies on physical interactions (non-covalent), such as hydrogen bonding and ionic interaction. Nuclear magnetic resonance analysis supports the notion that each component maintains its molecular identity, contributing to the unique properties of the ChCl/sulfanilic acid DES through the formation of non-covalent interactions. Several plausible interactions exist between sulfanilic acid and ChCl, with both acting as the HBD and HBA, respectively. Sulfanilic acid contributes its $–NH_2$ and $–SO_3H$ groups, whereas ChCl provides the –OH and $–Cl^-$ ion. Upon mixing, the Cl^- ion of ChCl forms strong hydrogen bonds with the $–SO_3H$ and –OH of groups of sulfanilic acid. These extensive hydrogen bonding interactions are believed to stabilize the resulting DES. Furthermore, owing to the acidic nature, the $–SO_3H$ groups facilitate proton (H^+) donation, which protonates the $–NH_2$ group of sulfanilic acid, resulting in the formation of an ammonium ion ($–NH_3^+$). This process creates ionic interactions with Cl^- or sulfonate ($–SO_3^-$) ions. Additionally, the –OH group of ChCl participates in hydrogen bonding with the oxygen atoms of the $–SO_3^-$, further reinforcing the structure of the ChCl/sulfanilic acid DES. These synergistic interactions possibly disrupt the crystalline structures of both sulfanilic acid and ChCl, thereby lowering the melting point and ultimately producing a highly polar solvent system for LA esterification [6]. This polar environment enhances the solvation of polar reactants like LA and ethanol [25], ensuring effective mixing and eliminating mass transfer limitations among the reactants and the catalyst. Moreover, the high catalyst acidity of the DES is attributed to the presence of various acid functional groups, including $–SO_3H$, which mainly promotes the reaction mechanism of LA esterification.

3.3 Reaction Mechanism and Performance of LA Conversion to EL

Figure 4 illustrates the sequential reaction mechanism of LA esterification to EL catalyzed by ChCl/sulfanilic acid as an acidic DES. In this reaction, $–SO_3H$ exhibits strong Brønsted acidity, dissociating H^+ to protonate the carbonyl oxygen of LA, thereby making the LA molecule more electrophilic (Figures 4(a–b)) [26]. The protonated LA facilitates the nucleophilic attack of ethanol to

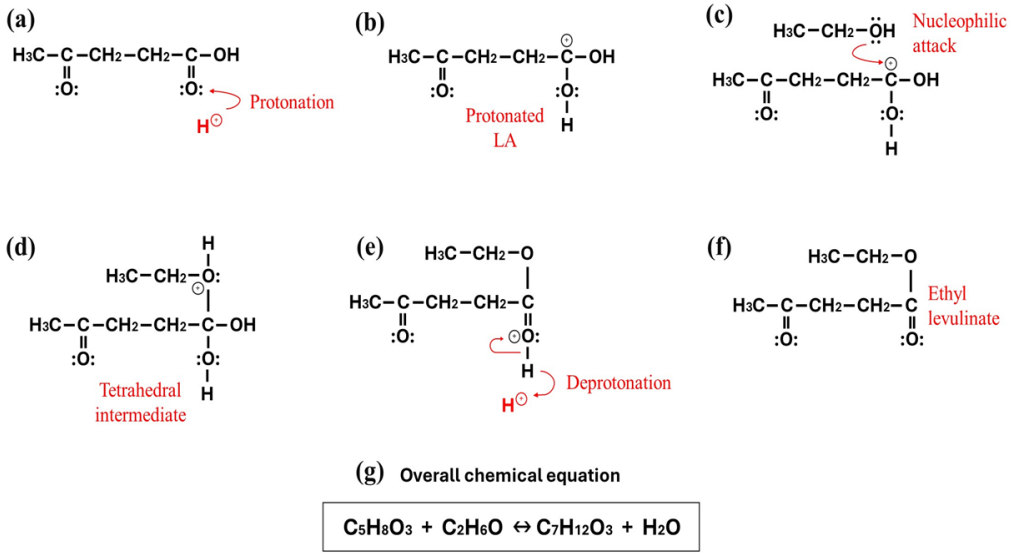

Figure 4. The reaction mechanism of LA esterification to EL catalyzed by ChCl/sulfanilic acid as an acidic DES

form a tetrahedral intermediate, which ultimately results in EL formation (Figures 4(c–f)) [27]. The overall chemical equation is presented in Figure 4(g). Moreover, the $–NH_3^+$ of sulfanilic acid acts as a secondary Brønsted acid, which also donates the H^+ to LA, prior to the similar subsequent mechanistic step that yields EL. In contrast to the Cl^- ion of ChCl, which does not exhibit acidic behavior, this ion plays an important role in stabilizing the H^+ released from the $–SO_3H$, –OH, and $–NH_3^+$ in the DES. The effective interaction between Cl^- and the dissociated H^+ enhances the proton donation capacity of the reaction system, ensuring the continuous availability of protons for catalytic activity. Collectively, these properties contribute to more efficient LA esterification by accelerating the protonation of LA, thus establishing ChCl/sulfanilic acid DES as a unique catalyst compared to other available homogeneous acid catalysts.

The effect of reaction parameters, including the molar ratio of LA to ethanol, the LA:DES ratio, and reaction time on the LA conversion is depicted in Figure 5. As shown in Figure 5(a), the conversion reached 95.2% at the LA-to-ethanol molar ratio of 1:7, the LA:DES ratio of 1:1, and the reaction time of 3 h. A similar trend was observed for the reaction with an LA:DES ratio of 1:0.4 and 3 h of reaction time, where the selected molar ratio was found to be 1:7. This finding aligns with previous research suggesting that the most effective molar ratio of LA to ethanol is 1:8 [28]. The results of LA conversion at various LA-to-ethanol molar ratios show that varying the amount of ethanol significantly affects the conversion of LA to EL. Further increases of ethanol in the reaction medium reduce LA conversion. This phenomenon was evident when the molar ratio of LA to ethanol was changed from 1:7 to 1:13, resulting in a reduction of LA conversion to 57.3%. The reduction is likely caused by an excess of ethanol, which decreases the concentration of LA. Such conditions may lead to solvent flooding on the acid sites, consequently reducing the adsorption of LA, and, indirectly, the conversion of LA to EL [29].

The effect of catalyst loading is a significant parameter to consider for LA esterification. In this study, DES was utilized as an acid catalyst, represented by the LA:DES ratio, with the results

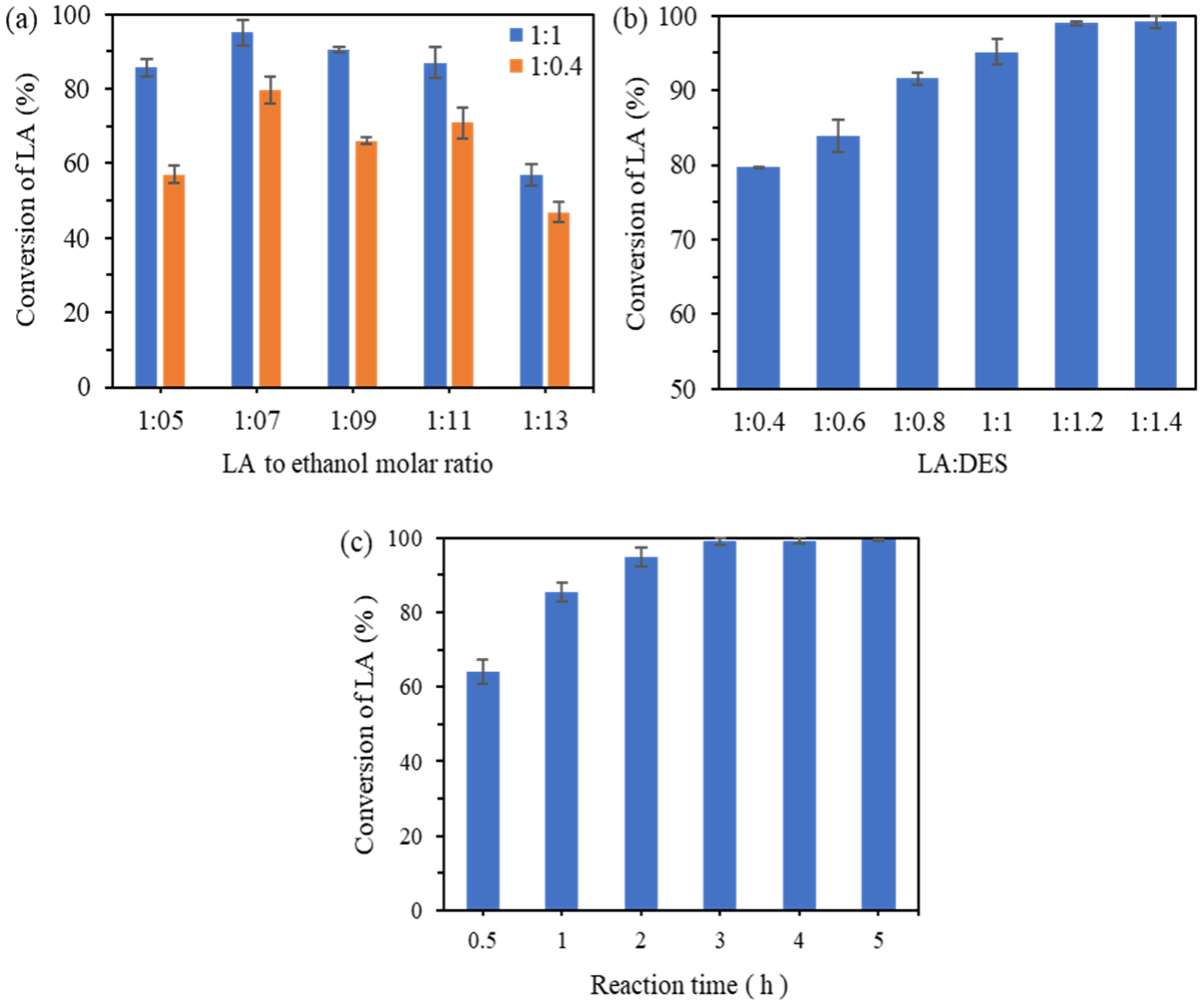

Figure 5. Parametric study of (a) LA-to-ethanol molar ratio at the LA:DES ratios of 1:1 and 1:0.4 (3 h, 80 °C); (b) LA:DES ratio (1:7 LA:ethanol molar ratio, 3 h, 80 °C); and (c) reaction time (1:7 LA:ethanol molar ratio, 1:1.2 LA:DES ratio, 80 °C) for the esterification of LA to EL

of LA conversion illustrated in Figure 5(b). The LA:DES ratios examined ranged from 1:0.4 to 1:1.4. It was observed that the conversion of LA increased from 79.7% to 99% as the ratio varied from 1:0.4 to 1:1.2. This indicates that an increase in the amount of DES as a catalyst enhances the reaction conversion. The optimum LA conversion was observed at a 1:12 LA:DES ratio, while further increases in the DES in the reaction mixture resulted in a minimal change, with the LA conversion of 99.2% obtained at a 1:14 LA:DES ratio. Sert [6] investigated the effect of an acidic DES, specifically ChCl combined with para-toluenesulfonic acid (ChCl/pTSA), for the conversion of LA to EL, where the catalyst amount was increased up to 5 wt.% to achieve an LA conversion of 99.8%. This remarkable result can be attributed to the high acidity of the DES prepared using a strong acid of pTSA. Additionally, 1-methyl imidazolium hydrogen sulfate [MIM][HSO_4] IL has been applied for the synthesis of butyl levulinate, where various molar ratios of LA to IL (catalyst loading) were studied, ranging from 1:0.06 to 1:0.75, and the optimum ratio was obtained at 1:0.25 with 89.6% of LA conversion [30]. It is important to note that increasing the catalyst loading in the reaction medium may also increase the viscosity of the reaction mixture, potentially restricting the rate of mass transfer [31]. This situation may cause the reaction to reach equilibrium, which may reduce the reactant conversion or product formation.

Figure 5(c) depicts the effect of reaction time on LA conversion. Based on the reaction time studied from 1 to 5 h, high LA conversion was observed at 3–5 h of reaction time. The LA conversion of 99% was obtained at 3 h of reaction time, and the conversion remained relatively stable, with a slight increase to 99.4% at 5 h of reaction time. A similar trend was also observed in a previous study, where the LA conversion or EL yield increased with time and reached equilibrium [3]. Li *et al.* [29] reported that prolonged reaction times do not result in a significant increase in the final product. This demonstrates that extending the reaction time for LA esterification is impractical, highlighting the necessity of establishing the optimum time. Thus, the optimum conditions for the esterification of LA with ethanol catalyzed by the DES were determined as follows: 1:7 of LA:ethanol molar ratio, 1:1.2 of LA:DES loading, and 3 h of reaction time at 80 °C.

The characteristics of the ChCl/sulfanilic acid DES support this reaction activity, where the high acidity of the DES contributes to high LA conversion to EL for the esterification reaction. The acidity of the DES is attributed to the presence of $–SO_3H$ groups. Furthermore, esterification can be conducted at 80 °C, as the DES demonstrates thermal stability up to 200 °C, allowing it to remain stable without degradation throughout the reaction.

The results of the LA conversion under optimum reaction conditions, as determined through acid-base titration, were further corroborated by GC-MS. This analysis serves as a reliable means of corroborating the titration results. Figures 6(a) and (b) present the GC-MS peak areas for the standard chemicals of EL and LA at a specific retention time. The EL peak was detected at approximately 19.0 min, while the LA peak was observed at around 20.0 min, based on the analysis of their corresponding standards. Focusing on EL and LA as the target compounds, Figure 6(c) displays the peaks that appear at the same retention times as those of the standard chemicals, thereby confirming the formation of EL and the presence of unreacted LA in the liquid product samples.

The results of EL yield (mol%) and LA conversion (%) from the synthesized liquid product under optimum reaction conditions quantified using GC-MS, along with LA conversion (%) from titration, are tabulated in Table 1. The results indicate that the GC-MS analysis achieved an EL yield of 90.6 mol% with 95.2% of LA conversion, which closely corresponds

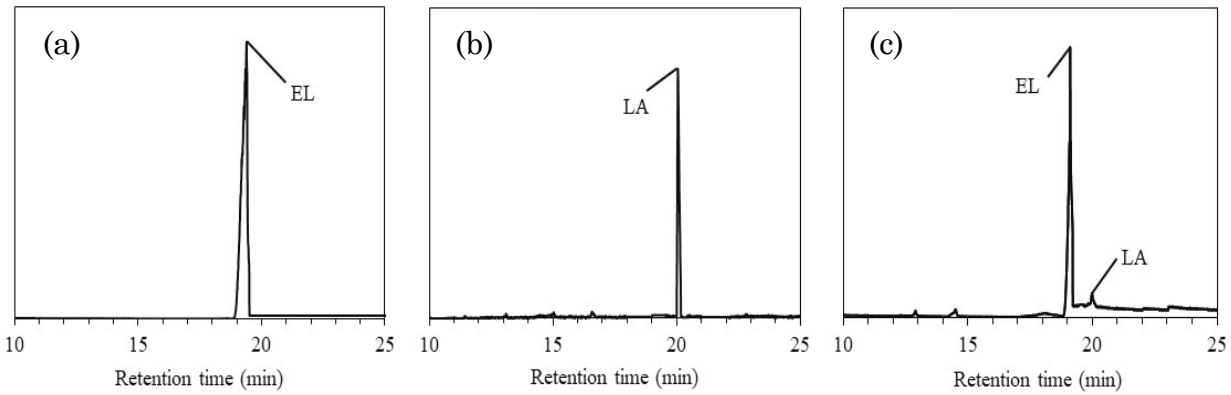

Figure 6. The GC-MS peak areas of standard chemicals at their respective retention times (min) for (a) EL and (b) LA, and (c) the detection of EL and LA peak areas in the synthesized liquid product sample

with the LA conversion determined through titration. The agreement between these two analytical methods can be used to validate the accuracy of the experimental data obtained from acid-base titration. Additionally, the high EL yield and LA conversion in this work highlight the potential application of an acidic DES as a catalyst in EL production, especially for LA esterification.

3.4 Comparative Study

The performance of ChCl/sulfanilic acid as an acidic DES prepared in this work was evaluated and compared to other available homogeneous catalysts reported in recent literature (Table 2). Mthembu *et al.* [32] employed 2.75 g of methanesulfonic acid (MsOH) with an ethanol-to-LA ratio of 10:1 (mL:g) and achieved an excellent EL yield of 92.2% over a prolonged reaction time of 5.25 h. Although MsOH has demonstrated effectiveness as a homogeneous catalyst in LA esterification, the reaction required excessive ethanol and a long reaction time to achieve a high product yield. In contrast, [6] utilized a DES prepared from ChCl/pTSA. A reaction mixture with a catalyst loading of 5 wt.% and 1:1 of ethanol-to-LA molar ratio resulted in exceptional LA conversion of 99.8% for 1 h of reaction time. However, the catalyst-to-reactant ratio (5 wt.%) was relatively high to attain high catalytic activity.

Silva *et al.* [33] reported the use of 1 mol% trivalent metal cation phosphomolybdic acid ($AlMo_{12}O_{40}$) and 9.6:0.5 (mL:g) of ethanol-to-LA ratio, resulting in 65.0% LA conversion at 6 h of reaction time. Pastore and D'Ambrosio [34] employed aluminum chloride hexahydrate ($AlCl_3.6H_2O$) with a catalyst loading of 5 mol%, ethanol-to-LA molar ratio of 1:1, and 2 h of reaction time, achieving an EL yield of 70%. Despite the relatively short reaction time, the high catalyst loading resulted in only a moderate EL yield. In contrast, the ChCl/sulfanilic acid DES investigated in this work demonstrated good reaction performance with 2 g of catalyst loading, 1:7 of ethanol-to-LA molar ratio, and 3 h of reaction time. This catalyst achieved high LA conversion of 99.0%, comparable to ChCl/pTSA. The balance between high LA conversion, low ethanol excess, and moderate reaction time highlights the advantages of the ChCl/sulfanilic acid DES relative to other homogeneous catalysts. This comparative analysis suggests that ChCl/sulfanilic acid DES represents a promising and efficient approach to homogeneous catalysis for LA esterification to synthesize EL.

4. Conclusions

In this study, the preparation of a ChCl/sulfanilic acidic DES to catalyze LA esterification to EL has been conducted successfully. This homogeneous catalyst exhibits unique properties, such as a polar solvent system to facilitate the solvation of reactants. Characterization analyses indicate that the catalyst exhibits thermal stability, supporting reaction conversions at temperatures up to 200 °C, in addition to a notable acidity of 2.89 mmol/g, which significantly facilitates the esterification of LA with ethanol to produce EL. In parametric studies, the optimum conditions were determined at a 1:7 molar ratio of LA to ethanol, 1:1.2 of LA:DES, and 3 h of reaction time at 80 °C. The effect of these parameters on the reaction resulted

Table 1. Liquid product obtained under optimum reaction conditions analyzed through acid-base titration and CG-MS.

Reaction performance	Liquid product analysis	
	Acid-base titration	GC-MS
EL yield (mol%)	-	90.6 ± 3.21
LA conversion (%)	99 ± 1.00	95.2 ± 1.23

Table 2. A comparison of various homogeneous acid catalysts in LA esterification to EL ([a] : LA conversion (%))

Catalyst	Reaction conditions			EL yield (%)	Ref.
	Catalyst loading	Molar ratio of ethanol to LA	Time (h)		
MsOH	2.75 g	10:1 (mL, g)	5.25	92.2	[32]
ChCl/pTSA	5 wt.%	1:1 molar ratio	1	99.8[a]	[6]
$AlMo_{12}O_{40}$	1 mol%	9.6:0.5 (mL, g)	6	65.0[a]	[33]
$AlCl_3.6H_2O$	5 mol%	1:1 molar ratio	2	70	[34]
ChCl/sulfanilic acid	2 g	1:7 molar ratio	3	99.0[a]	This work

in excellent LA conversion of up to 99%. The ChCl/sulfanilic acid DES demonstrates considerable potential as a catalyst, exhibiting performance comparable to other homogeneous catalysts, and is feasible for applications in large-scale EL synthesis.

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