FACULTY OF ENGINEERING
AND ARCHITECTURE

Preparation of ionic liquids and deep eutectic solvents for the chemical valorisation of polylactide waste

Maarten Duerinck
Student number: 01605247

Supervisors: Prof. dr. ir. Jeriffa De Clercq, Prof. Amparo Chafer (Universitat de Valéncia)
Counsellor: Prof. José Badia (Universitat de Valéncia)

Master's dissertation submitted in order to obtain the academic degree of
Master of Science in de industriële wetenschappen: chemie

Academic year 2019-2020

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Preamble

The experimental work was planned to last until mid-May, this consisted in the synthesis of the protic ionic liquids (2-hydroxyethyl ammonium acetate [2-HEAA], bis-(2-hydroxyethyl) ammonium acetate [BHEAA] and tris-(2-hydroxyethyl) ammonium acetate [THEAA]) and the L-mentnol:decanoic acid deep eutectic solvent (DES), their characterization, the measurement of their water content and thermophysical properties and the application of the PILs as catalysts in the hydrolysis of poly (lactic acid). However, this work was cut short due to the Corona-outbreak. Every experimental procedure involving the protic ionic liquid (PIL) 2-HEAA was performed, but for the DES, only the synthesis was performed. For the PILs BHEAA and THEAA, it was not even possible to perform their synthesis and none of the PILs were able to be applied as catalysts in the hydrolysis of poly (lactic acid). Besides this, the Corona outbreak forced me to leave Valencia and return back to Belgium. This means that even if we were able to return to the laboratory after a few months, I could not perform any experimental work anymore.

To compensate for this loss, more focus was put on the literature study and the description of the methods that were used or would have been used in this work. As soon as Mrs. Chafer and Mr. Badia were able to go back to the laboratory, they tested the hydrolysis of poly (lactic acid) with 2-HEAA as catalyst. Thanks to these results, I was still able to discuss all aspects of the thesis.

Abstract

In recent years, a lot of research has been put into finding greener alternatives for volatile organic Compounds (VOCs). One of these alternatives that has gained a lot of attention is the group of the ionic liquids. This group of solvents is a promising alternative for VOCs due to their low vapor pressure, their non-flammability and thermal and chemical stability. However, these solvents have a high cost, require a high degree of purity and their toxicity has yet to be ascertained. Recently, the attention has been shifted towards deep eutectic solvents (DES). These solvents have similar thermophysical properties, but they eliminated the above-mentioned disadvantages of the ionic liquids.

In this context, the aim of this work was to synthesize and characterize alkanolamine-based protic ionic liquids (PIL) and a L-menthol-decanoic acid DES. The effectiveness of the synthesized PILs will be showcased as solvent/catalyst in the chemical valorization of poly(lactic acid) (PLA), a future high-consumed bioplastic.

For this purpose, the most appropriate methods of synthesis for these solvents were selected by comparing different methodologies in the literature and checked via characterization. For the PIL, 2-hydroxyethyl ammonium acetate, this was done by measuring its thermophysical properties and its FT-IR, H-NMR and C-NMR spectra.

The refractive index of 2-HEAA was measured at 25 °C and density at 20 °C. The value of the refractive index always varied around 1.47009 ± 0.00006 and the measured values of the density were around 1.54844 ± 0.000023 g/cm^3. These values were then compared with values reported in literature. The measured values showed to be similar to some of the values mentioned in the literature. When comparing the literature values with each other they showed large differences. Due to this fact, it is not possible to conclude that the synthesis was successful based on the thermophysical properties alone, but the measured values can still be considered reliable. The FT-IR and the NMR spectra can be used to determine if the synthesis was successful without a margin of error.

The FT-IR, H-NMR and C-NMR spectra recorded in this study are practically identical with the ones reported in the literature, with the only difference in the H-NMR spectra being the result of different solvents used in this study and the one reported in literature. This leads to the conclusion that the synthesis of the PIL was successful.

The DES was produced with the molar ratio of 35:65 (L-menthol:decanoic acid), which was close to the optimal ratio (65:35). Even with this suboptimal molar ratio, it showed to be immiscible with water, which is one of the properties that only few DES possess. Together with the fact that the DES was liquid at room temperature, this confirmed that the synthesis itself is successful and that the synthesis method would be the appropriate one if in future synthesis the correct mixing ratio of 65:35 is used.

Finally, the hydrolysis of PLA was showcased with the produced PIL as catalyst and the conditions described by *McKeown et al. (2020)* (temperature of 130 °C, ratio of 12:2:1 [water/PLA/IL] and reaction time of 2 hours). First these conditions were tested with an aprotic ionic liquid (AIL), 1-ethyl-3-methylimidazolium acetate ([Emim][Oac]), that was described in the work of *Song et al. (2014)*. However, this did not give the 90.86% conversion of PLA into lactic acid that was described in this work. After increasing the reaction time for 2 hours to 5.5 hours, reducing the amount and the size of PLA from 2 g to 1 g and from 5 mm to 0.5 mm respectively, the results were much better, but the AIL did also decompose. When taking the decomposition into account, the reaction with the longer reaction time and a smaller amount of PLA gave a conversion into lactic acid of 95.56%.

Afterwards, the hydrolysis of PLA was performed with the synthesized 2-HEAA as catalyst. This reaction gave a conversion of 97.71% which is better than the best result obtained by *Song et al. (2014)*, which was 93.93% for the AIL 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]). However, it has to be noted that this AIL was only given 2 hours of reaction time. If it was given the 5.5 hours used in this work it might have given similar or even better conversions. This makes it difficult to say which ionic liquid gives the best results. The obtained result for 2-HEAA was slightly better than the result that was obtained for the [Emim][Oac]. Even though the conversions are similar, it is advised to use the PIL instead of the AIL, because it has a greener character and a lower production cost.

Abstract

De afgelopen jaren is er veel onderzoek gedaan naar het vinden van groenere alternatieven voor vluchtige organische stoffen (VOS). Een van deze alternatieven die veel aandacht heeft gekregen is de groep van de ionische vloeistoffen. Deze groep oplosmiddelen is een veelbelovend alternatief voor VOS vanwege hun lage dampspanning, hun onbrandbaarheid en thermische en chemische stabiliteit. Deze oplosmiddelen hebben echter hoge kosten, vereisen een hoge mate van zuiverheid en hun toxiciteit moet nog worden vastgesteld. Onlangs is de aandacht verschoven naar diep eutectische oplosmiddelen (DES). Deze oplosmiddelen hebben vergelijkbare thermo-fysische eigenschappen, maar elimineren de bovengenoemde nadelen van de ionische vloeistoffen.

In deze context was het doel van dit werk het synthetiseren en karakteriseren van op alkanolamine gebaseerde protische ionische vloeistoffen (PIL) en een L-menthol-decaanzuur DES. De effectiviteit van de gesynthetiseerde PIL's zal worden getoond als oplosmiddel / katalysator bij de chemische valorisatie van poly (melkzuur) (PLA), een toekomstig veel geconsumeerd bioplastic.

Voor dit doel werden de meest geschikte synthesemethoden voor deze oplosmiddelen geselecteerd door verschillende methodologieën in de literatuur te vergelijken en deze methode werd gecontroleerd via karakterisering. Voor het PIL, 2-hydroxyethylammoniumacetaat werd dit gedaan door de thermofysische eigenschappen ervan en de FT-IR-, H-NMR- en C-NMR-spectra te meten.

De brekingsindex van 2-HEAA werd gemeten bij 25 ° C en dichtheid bij 20 ° C. De waarde van de brekingsindex varieerde altijd rond 1.47009 ± 0.00006 en de gemeten dichtheidswaarden waren rond 1.54844 ± 0.000023 g / cm^3. Deze waarden werden vervolgens vergeleken met waarden vermeld in de literatuur. De gemeten waarden bleken vergelijkbaar te zijn met enkele van de in de literatuur genoemde waarden. Bij het vergelijken van de literatuurwaarden met elkaar lieten ze grote verschillen zien. Vanwege dit feit is het niet mogelijk om te concluderen dat de synthese succesvol was op basis van alleen de thermofysische eigenschappen, maar de gemeten waarden kunnen nog steeds als betrouwbaar worden aanschouwd. De FT-IR en de NMR-spectra kunnen worden gebruikt om te bepalen of de synthese succesvol was zonder een foutmarge.

De FT-IR-, H-NMR- en C-NMR-spectra die in dit onderzoek zijn opgenomen, zijn praktisch identiek aan die in de literatuur, met het enige verschil in het H-NMR-spectrum het gevolg van de verschillende oplosmiddelen die in dit onderzoek en in de literatuur zijn gebruikt. Dit leidt tot de conclusie dat de synthese van de PIL succesvol was.

De DES werd geproduceerd met een molverhouding van 35:65 (L-menthol: decaanzuur), wat dicht bij de optimale verhouding lag (65:35). Zelfs met deze suboptimale molverhouding bleek het niet mengbaar met water, wat een van de eigenschappen is die slechts weinigen DES bezitten. Dit en het feit dat de DES vloeibaar was bij kamertemperatuur bevestigde dat de synthese zelf succesvol is en dat de synthesemethode de juiste zou zijn als in de toekomstige synthese de juiste mengverhouding van 65:35 wordt gebruikt.

Ten slotte werd de hydrolyse van PLA getoond met de geproduceerde PIL als katalysator en de omstandigheden beschreven door *McKeown et al. (2020)* (temperatuur van 130 ° C, verhouding 12: 2: 1 [water/PLA/IL] en reactietijd van 2 uur). Eerst werden deze omstandigheden getest met een aprotische ionische vloeistof (AIL), 1-ethyl-3-methylimidazoliumacetaat ([Emim] [Oac]), die werd beschreven in het werk van *Song et al. (2014)*. Dit leverde echter niet de 90,86% omzetting van PLA in melkzuur op die in dit werk werd beschreven. Na het verhogen van de reactietijd van 2 uur tot 5,5 uur, het verminderen van de hoeveelheid en de grootte van PLA van respectievelijk 2 g tot 1 g en van 5 mm tot 0,5 mm, waren de resultaten veel beter, maar de AIL ontbond ook. Rekening houdend met de ontleding gaf de reactie met de langere reactietijd en een kleinere hoeveelheid PLA een omzetting in melkzuur van 95,56%.

Daarna werd de hydrolyse van PLA uitgevoerd met de gesynthetiseerde 2-HEAA als katalysator. Deze reactie gaf een conversie van 97,71%, wat beter is dan het beste resultaat verkregen door *Song et al. (2014)*, wat 93,93% was voor het AIL 1-butyl-3-methylimidazoliumacetaat ([Bmim] [OAc]). Er moet echter worden opgemerkt dat deze AIL slechts 2 uur reactietijd kreeg. Als het de 5,5 uur had gekregen die in dit werk zijn gebruikt, zou het vergelijkbare of zelfs betere conversies hebben opgeleverd. Dit maakt het moeilijk om te zeggen welke ionische vloeistof het beste resultaat geeft. Het verkregen resultaat voor 2-HEAA was iets beter dan het resultaat dat werd verkregen voor de [Emim] [Oac]. Hoewel de conversies vergelijkbaar zijn, wordt geadviseerd om de PIL te gebruiken in plaats van de AIL, omdat deze een groener karakter heeft en lagere productiekosten.

Abstract

En los últimos años, se han realizado muchas investigaciones para encontrar alternativas más ecológicas para los compuestos orgánicos volátiles (COV). Una de estas alternativas que ha llamado mucho la atención es el grupo de los líquidos iónicos. Este grupo de solventes es una alternativa prometedora para los COV debido a su baja presión de vapor, su no inflamabilidad y su estabilidad térmica y química. Sin embargo, estos solventes tienen un alto costo, requieren un alto grado de pureza y su toxicidad aún no se ha determinado. Recientemente, la atención se ha desplazado hacia los solventes eutécticos profundos (DES). Estos solventes tienen propiedades termofísicas similares, pero eliminaron las desventajas mencionadas anteriormente de los líquidos iónicos.

En este contexto, el objetivo de este trabajo fue sintetizar y caracterizar líquidos iónicos próticos a base de alcanolamina (PIL) y un ácido L-mentol-decanoico DES. La eficacia de los PIL sintetizados se mostrará como un disolvente / catalizador en la valorización química del poli (ácido láctico) (PLA), un futuro bioplástico ampliamente consumido.

Para este propósito, los métodos de síntesis más adecuados para estos solventes se seleccionaron comparando diferentes metodologías en la literatura y este método se verificó mediante caracterización. Para el PIL, acetato de 2-hidroxietilamonio, esto se realizó midiendo sus propiedades termofísicas y los espectros FT-IR, H-NMR y C-NMR.

El índice de refracción de 2-HEAA se midió a 25 ° C y la densidad a 20 ° C. El valor del índice de refracción siempre varió alrededor de 1.47009 ± 0.00006 y los valores de densidad medidos fueron alrededor de 1.54844 ± 0.000023 g / cm^3. Estos valores se compararon con los valores reportados en la literatura. Se encontró que los valores medidos eran comparables a algunos de los valores informados en la literatura. Al comparar los valores de la literatura entre sí, mostraron grandes diferencias. Debido a este hecho, no es posible concluir que la síntesis fue exitosa basada únicamente en las propiedades termofísicas, pero los valores medidos aún pueden considerarse confiables. Los espectros FT-IR y NMR pueden usarse para determinar si la síntesis fue exitosa sin un margen de error.

Los espectros FT-IR, H-NMR y C-NMR registrados en este estudio son prácticamente idénticos a los informados en la literatura, siendo la única diferencia en los espectros H-NMR el resultado de diferentes solventes utilizados en este estudio y el uno reportado en la literatura. Esto lleva a la conclusión de que la síntesis de la PIL fue exitosa.

El DES se produjo con la relación molar de 35:65 (L-mentol: ácido decanoico), que estaba cerca de la relación óptima (65:35). Incluso con esta relación molar subóptima, demostró ser inmiscible con agua, que es una de las propiedades que solo poseen unos pocos DES. Junto con el hecho de que el DES era líquido a temperatura ambiente, esto confirmó que la síntesis en sí misma es exitosa y que el método de síntesis sería el apropiado si en una síntesis futura se usa la relación de mezcla correcta de 65:35.

Finalmente, la hidrólisis de PLA se mostró con el PIL producido como catalizador y las condiciones descritas por *McKeown et al. (2020)* (temperatura de 130 ° C, relación de 12: 2: 1 [agua / PLA / IL] y tiempo de reacción de 2 horas). Primero, estas condiciones se probaron con un líquido iónico aprótico (AIL), acetato de 1-etil-3-metilimidazolio ([Emim] [Oac]), que se describió en el trabajo de *Song et al. (2014)* Sin embargo, esto no dio la conversión del 90.86% de PLA en ácido láctico que se describió en este trabajo. Después de aumentar el tiempo de reacción durante 2 horas a 5,5 horas, reducir la cantidad y el tamaño de PLA de 2 ga 1 gy de 5 mm a 0,5 mm respectivamente, los resultados fueron mucho mejores, pero el AIL también se descompuso. Al tener en cuenta la descomposición, la reacción con el tiempo de reacción más largo y una cantidad menor de PLA dio una conversión en ácido láctico del 95,56%.

Posteriormente, la hidrólisis de PLA se realizó con el 2-HEAA sintetizado como catalizador. Esta reacción dio una conversión de 97.71% que es mejor que el mejor resultado obtenido por Song et al. (2014), que fue del 93,93% para el acetato de 1-butil-3-metilimidazolio AIL ([Bmim] [OAc]). Sin embargo, debe tenerse en cuenta que esta AIL solo recibió 2 horas de tiempo de reacción. Si se le dieron las 5.5 horas utilizadas en este trabajo, podría haber dado conversiones similares o incluso mejores. Esto hace que sea difícil decir qué líquido iónico da los mejores resultados. El resultado obtenido para 2-HEAA fue ligeramente mejor que el resultado obtenido para [Emim] [Oac]. Aunque las conversiones son similares, se recomienda utilizar el PIL en lugar del AIL, ya que tiene un carácter más ecológico y un menor costo de producción.

Extended Abstract

Abstract **The interest in protic ionic liquids and deep eutectic solvents has increased in the recent years. This a direct result of the search for greener, non-volatile alternatives for volatile organic solvents. The aim of this work was to synthesize a series of alkanolamine-based protic ionic liquids and a menthol-based deep eutectic solvent for applications that can be used in laboratories and the industry. These applications include the use in the pretreatment of biomass to make the cellulose more accessible for enzymatic reactions, as catalyst in the hydrolysis of poly (lactic acid) and as solvent in the liquid-liquid extraction of aqueous alcohol mixtures. To achieve this goal the most suited method of synthesis was selected by comparing different methods reported in literature and applied. The synthesized solvents were characterized to confirm the synthesis method. For the protic ionic liquid 2-hydroxyethyl ammonium acetate (2-HEAA) and the deep eutectic solvent L-menthol:decanoic acid, the characterization confirmed that the synthesis was in fact successful. The refractive index and the density of 2-HEAA were respectively 1.47009 ± 0.00006 at 25 °C and 1.154844 ± 0.000023 g/cm^3 at 20 °C. Finally, the synthesized 2-HEAA was showcased in the hydrolysis of poly (lactic acid).**

Keywords **Protic ionic liquid; Alkanolamines; Deep eutectic solvent; Menthol; Poly (lactic acid); Hydrolysis**

I. INTRODUCTION

In the recent years, a lot of research has been put into finding greener alternatives for volatile organic solvents (VOCs). One of these alternatives that has gained a lot of attention is the group of the ionic liquids. Ionic liquids (ILs) are salts that are in a liquid state at temperatures below 100 °C. This group is considered as a promising alternative mainly due to their low vapor pressure, but also due to their non-flammability and their chemical and thermal stability. One of the most notable facts about these solvents is that their properties can be tuned for specific applications by changing the cation and/or anion [1], [2]. The most commonly used cations and some of the possible anions that can be combined with them to form ILs are given in Figure 1, together with their hydrophobic nature.

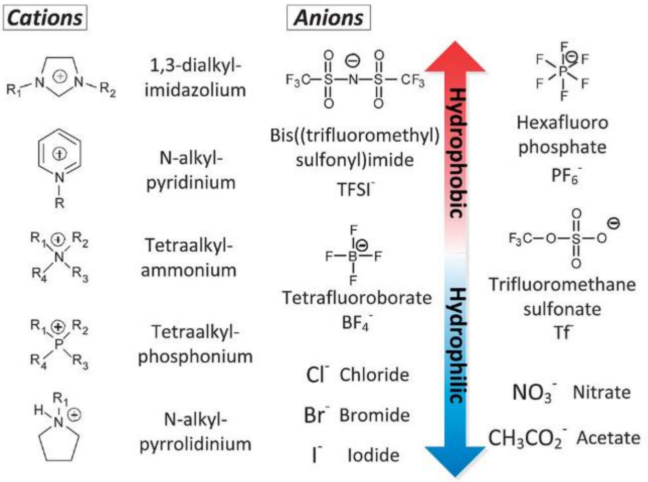

Figure 1: Structures of most commonly used cations and anions that can be combined to form ionic liquids

Even though ionic liquids might be considered as ‘green’ alternatives, there are still some disadvantages that make them not ideal alternatives. These disadvantages are the following: the high associated cost, the required high degree of purity and a toxicity and biodegradability that has yet to be ascertained.

Recently, the attention has been shifted towards deep eutectic solvents (DESs). These solvents are mixtures of one or more hydrogen bond donors (HBDs) and one or more hydrogen bond acceptors (HBAs) at the eutectic composition. They have the same beneficial properties as the ionic liquids, but DESs eliminate these disadvantages since most of the DESs are composed of compounds that are gained from renewable resources [3]. These most commonly used HBDs and HBAs for the synthesis of deep eutectic solvents are shown in Figure 2.

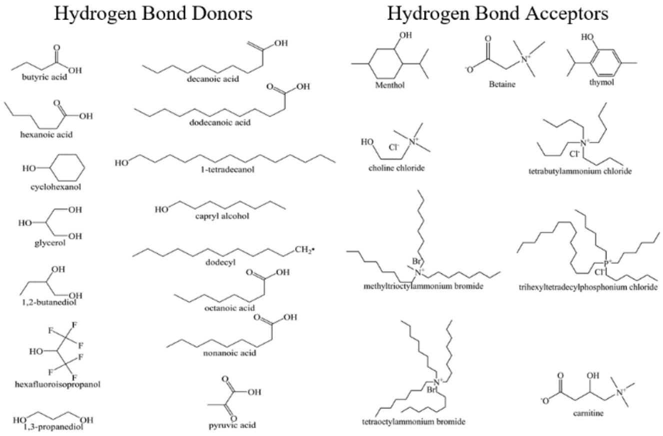

Figure 2: Most commonly used hydrogen bond donors (left) and hydrogen bond acceptors (right) for the synthesis of DES.

In this context, the main goal of this work is to produce and characterize alkanolamine-based protic ionic liquids (PILs) and a L-menthol-based based DES for application like: the use in the pretreatment of biomass, as catalyst in the hydrolysis of poly(lactic acid) and as solvent for the liquid-liquid extraction of aqueous alcohol mixtures.

II. Materials and methods

Various methods of synthesis found in the literature were compared to find the most appropriate method to synthesize and purify the desired solvents. The most appropriate ones were then adjusted.

A. *2-hydroxyethyl ammonium acetate*

For the PIL 2-hydroxyethyl ammonium acetate (2-HEAA) the most efficient method of synthesis involved the neutralization reaction of 2-hydroxyethyl amine (Sigma-Aldrich, ≥ 99.5%) with acetic acid (Sigma-Aldrich, ≥ 99%). The 2-hydroxyethyl amine was first loaded into a three-necked round bottom flask. The flask is then mounted in a thermostatic bath (RTE-200; Neslab) for cooling, which is kept at 20 °C to avoid crystallization of the PIL. The flask is then equipped with a reflux condenser to condensate the reagents in the gas phase. The reaction is started by adding a small excess of the acid in a dropwise manner to ensure full conversion of the 2-hydroxyethyl amine. After the addition, the mixture is kept stirring for 24 hours at 20 °C to ensure a complete as possible conversion. The completion of the reaction was monitored with a refractometer (Abbemat; Anton Paar) and was considered complete when the refractive index approached the literature values and when there were no solids or crystals in the ionic liquid. The purification was performed via vacuum drying at 100 °C for 6 to 8 hours with methanol entrainment at 4 hours and 6 hours to increase the efficiency of the purification.

B. *Bis-(2-hydroxyethyl) ammonium acetate and Tris-(2-hydroxyethyl) ammonium acetate*

The most efficient method of synthesis for bis-(2-hydroxyethyl) ammonium acetate (BHEAA) and for tris-(2-hydroxyethyl) ammonium acetate (THEAA) is similar to the one of 2-HEAA, but respectively with the neutralization of bis-(2-hydroxyethyl)amine and tris-(2-hydroxyethyl)amine with a slight excess of acetic acid to ensure a complete as possible conversion. The only other difference is the temperature of the thermostatic bath. This is 30 °C for BHEAA and 25 °C for THEAA to prevent the ionic liquid from crystalizing. The purification is performed in the same manner as described for 2-HEAA.

C. *L-menthol:Decanoic acid DES*

The most appropriate method for the synthesis of the L-menthol:decanic acid DES is by mixing L-menthol (Sigma-Aldrich, ≥99%) and decanoic acid (Sigma-Aldrich, ≥98%) in a molar ratio of 65:35 and then heating the mixture until a homogenous liquid is obtained like *Martins et al.(2018)* [4]suggests. However, due to an error, a wrong molar ratio of 35:65 was used. The temperature was then gradually increase from 40 °C in steps of 2 °C until 50 °C. Once both compounds were in a liquid state, a magnetic stirrer was added to the mixture and it was kept stirring at 260 rpm until a homogenous liquid was obtained. Afterwards, the DES would be purified via vacuum drying for 2 days at a temperature of 60 °C as suggested by *Verma et al.(2018)* [5].

III. Results and Discussion

A. *Thermophysical properties of 2-HEAA*

The refractive index (RI) (n_D) of 2-HEAA at 25 °C and the density (ρ) at 20 °C were compared the literature. The refractive index of 2-HEAA was 1.47009 ± 0.00006 and the density was 1.54844 ± 0.0000223 g/cm^3. This can be seen in Table 1 and Table 2 respectively. The literature RI-value closest to the measured ones was reported by *Greaves et al.(2006)* at 25 °C (1.469 ± 0.0005) [6] and the literature density closest to the measured densities is reported by *Hosseini et al.(2019)* at 20 °C (1.559 ± 0.000021 g/cm^3) [7].

The measured values showed no significant differences between each other. The measured values showed to be similar to some of the values mentioned in the literature. When comparing the literature values with each other they showed large differences as can be seen for the density in Table 2 and in Table 1 for the refractive index. Due to this fact, it is not possible to conclude that the synthesis was successful based on the thermophysical properties alone, but the measured values can still be considered reliable. The FT-IR and the NMR spectra can be used to determine if the synthesis was successful without a margin of error.

Table 1: Measured and literature refractive indexes for 2-HEAA

$n_{D,\ this\ work}$	$n_{D,\ literature}$	Source
1.47008	1.143682*	[8]
1.46997	1.4711*	[7]
1.47000	1.4754	[9]
1.47007	1.469	[6]
1.47010	-	-
1.47008	-	-

*: these values were measured at 20 °C.

Table 2: Measured and literature densities values for 2-HEAA

$\rho_{this\ work}$ (g/cm^3)	$\rho_{literature}$ (g/cm^3)	Source
1.155057	1.151	[10]
1.154872	1.1559	[7]
1.154602	1.14866	[11]

B. *Characterization of the solvents*

After the synthesis, the synthesis method of the solvents was checked by their characterization. This was done for 2-HEAA with FT-IR, H-NMR and C-NMR and for the DES by checking one of its properties.

1) *FT-IR spectrum of 2-HEAA*

The FT-IR spectrum recorded in this study was is similar to the one recorded in the work of *Rocha et al.(2017)* [9]. Both recorded spectra can be seen in Figure 3.

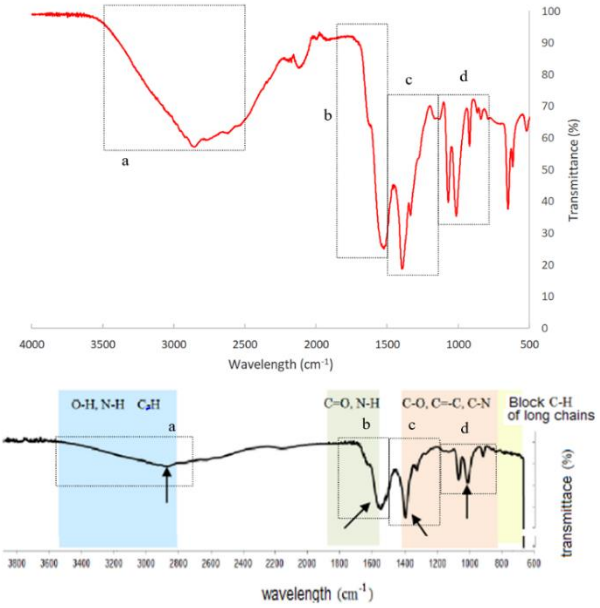

Figure 3: 2-HEAA FT-IR spectra recorded in this work (top) and by *Rocha et al.(2017)*(bottom).

Both spectra showed a broad band in the range of 3500 to 2500 cm^{-1} (a), which is characteristic for amine structures. The hydroxyl, methyl and methylene stretching vibrations are also incorporated in this band. The band between 1800 and 1500 cm^{-1} is considered a combined band of the C=O stretching and N-H curvature vibrations.

The bands between 1500 and 800 cm^{-1} are caused by the C-O and the C-N bonds. The band ranging from 1500 to 1200 cm^{-1} is the result of the C-O stretching vibrations and the band from 1200 to 800 cm^{-1} is the result of C-N stretching vibrations.

The only band that might indicate the presence of some sort of impurity is the one between 800 – 500 cm^{-1}. This impurity is then most likely a compound with a disubstituted cis-double bond (800 - 680 cm^{-1}) or a monosubstituted aromatic compound (680 cm^{-1} and at ± 750 cm^{-1}). The H- and C-NMR can give more information about these possible impurities. Besides this one band, the spectra show a significant resemblance which indicates that the synthesis was successful.

2) *H-NMR spectrum of 2-HEAA*

The H-NMR spectrum recorded in this work is, just like the FT-IR spectrum, similar to the spectrum recorded by *Rocha et al. (2017)* [9]. Both spectra are given in Figure 4.

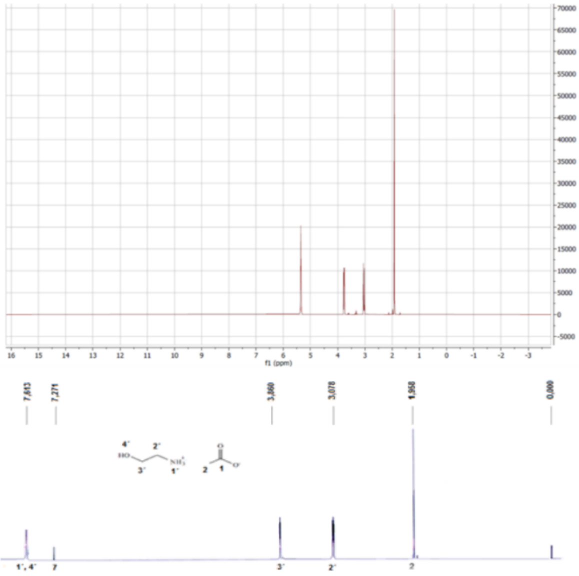

Figure 4: 2-HEAA H-NMR spectra recorded in this work (top) and by *Rocha et al. (2017)* (bottom).

The first peak (starting from the right) at δ = ± 2 ppm is most likely caused by the hydrogens in the methyl groups. The following peaks at δ = 3 ppm and δ = 3.8 ppm are most likely the result of the hydrogens in the methylene groups respectively next to the ammonium group and the hydroxyl group.

The other peaks of both spectra are different. In the spectrum recorded in this work, the peak located at δ = ± 5.4 ppm is most and likely caused by the hydrogen in the hydroxyl groups. Normally, this peak would appear around δ = 0.5 ppm, but the hydrogen is strongly deshielded by the formation of hydrogen bonds with the solvent deuterated methanol.

The peaks in the spectrum by *Rocha et al.* at δ = 7.2 ppm and δ = 7.6 ppm are probably caused by the solvent used for the recording of the H-NMR spectrum, which was in this case deuterated chloroform.

The recorded spectrum shows no other peaks besides the peaks from the solvent and the 2-HEAA. This leads to the assumption that the synthesis was successful.

3) *C-NMR spectrum of 2-HEAA*

The recorded C-NMR spectrum is the same as the spectrum of *Rocha et al. (2017)* [9], which was expected since both spectra were recorded for the same component in the same solvent (deuterated methanol). Both spectra are given in Figure 5.

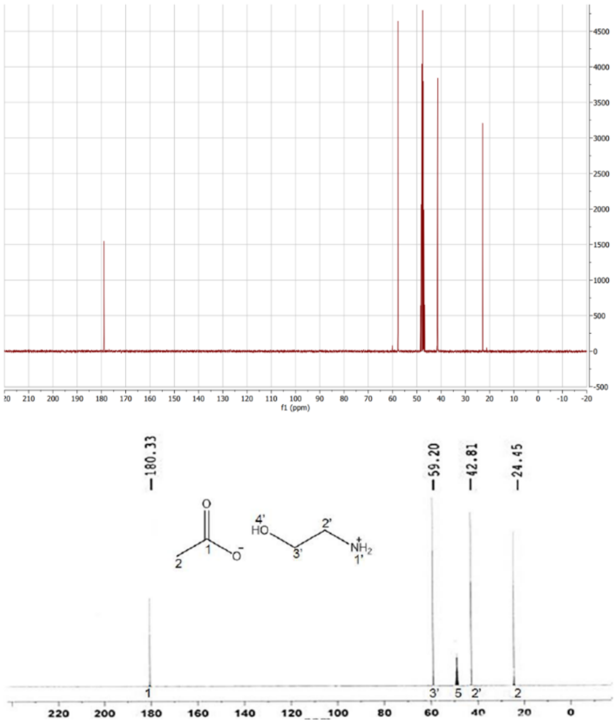

Figure 5: 2-HEAA C-NMR spectra recorded in this work (top) and by *Rocha et al. (2017)* (bottom).

The first peak (starting from the right) is caused by the carbon in the methyl group on the acetate ion. The next peak is the result of the carbon from the methylene group next to the ammonium group. The following peak is the result of the carbon in the deuterated methanol. The last two peaks are caused by respectively the carbon in the methylene group next to the hydroxyl group and the carbon in the carboxyl group.

There are no other peaks present than the peaks caused by 2-HEAA and the solvents. This leads to the conclusion that there are no significant impurities present, so the synthesis method can be considered successful.

4) *L-menthol:decanoic acid DES*

The synthesis of the L-menthol:decanoic acid DES is checked by testing one of its properties. The property that was chosen is the immiscibility with water since the goal is to apply it as solvent in the extraction of aqueous alcohol mixtures and since there are only a few DESs that do possess this property.

After mixing a small amount of the DES with water, it did in fact appear to possess this property. The fact that the DES was liquid at room temperature together with this property give a good indication that the synthesis itself was successful and that in future synthesis just the proper molar ratio has to be used.

IV. HYDROLYSIS OF PLA

One of the aprotic ionic liquids (AILs) ([Emim][OAc]) described by *Song et al. (2014)* [12] was tested as catalyst in the hydrolysis of PLA. The conditions were described in *McKeown et al. (2020)* [13]: a mass ratio of 12:2:1 (water:PLA:IL), a temperature of 130 °C and a reaction time of 2 hours. A conversion of about 90.86% was expected, but after the reaction, about a third of the initial PLA was still left, which indicates that this conversion is not achieved. The results after changing the reaction time to 5.5 hours and the amount of PLA to 1 g were much better. During this experiment all other conditions and the ratios were kept the same. The main problem now is that during this experiment the ionic liquid also decomposed, which interfered with the titration that is used to determine the amount of lactic acid. After this experiment, there were always two pressure tubes prepared: one with water, PLA and IL in the mass ratio of 6:1:0.5 and one with only water and IL in the mass ratio of 6:1. The latter was titrated and used as a correction for the decomposition of the ionic liquid. A conversion of 95.56% was achieved in the experiment with the following conditions: a mass ratio of 6:1:0.5 (water:PLA:IL), a temperature of 130 °C and a reaction time of 5.5 hours.

The hydrolysis was performed with a mass ratio of 6:1:0.5 (water:PLA:IL), a temperature of 130 °C and a reaction time of 5.5 hours, but this time with the synthesized PIL 2-HEAA. A conversion of 97.71% was achieved with this PIL, which was better than the best result obtained by *Song et al.*[12]. This result was obtained for the AIL [Bmim][OAc] at a mass ratio of 12:2:1 (water:PLA:IL), a temperature of 130 °C and a reaction time of 2 hours and had a value of 93.93%. The result obtained in this work is better, but it has to be noted that the reaction time was much shorter. If the reaction time was the same, the hydrolysis [Bmim][OAc] might have given a conversion that was similar or even better.

The conversion obtained for 2-HEAA was slightly better than the conversion obtained for the AIL [Emim][OAc] in this work. It is advised to use the PIL instead of the AIL, even though they have a similar conversions. This is because PILs have a greener character and have a lower production cost than AILs.

V. CONCLUSION

For the application of these protic ionic liquids and deep eutectic solvents in the pretreatment of biomass, the hydrolysis of poly (lactic acid) or the liquid-liquid extraction of aqueous alcohol mixtures, it is important to use the proper synthesis method to obtain the desired properties for these applications.

The measured values for the thermophysical properties are similar to some of the values reported in the literature, but there are large discrepancies between the values reported in the literature. Due to these discrepancies it is not possible to determine if the synthesis was successful based on the values of the thermophysical properties alone. The FT-IR and the NMR spectra can be used to determine if the synthesis was successful without a margin of error.

The characterization of 2-hydroxyethyl ammonium acetate via FT-IR, H-NMR and C-NMR showed that the synthesis method used in this work is the proper one. The immiscibility of the deep eutectic solvent with water together with the fact that is was liquid at room temperature gave a good indication that the synthesis itself was successful. This means that the method of synthesis would be the proper one if the correct mixing ratio of L-methol:decanoic acid is utilized.

The testing of the hydrolysis of poly (lactic acid) with the described AIL [Emim][OAc] as catalyst at a mass ratio of 12:2:1 (water:PLA:IL), a temperature of 130 °C and a reaction time of 2 hours did not give the expected 90.86% conversion. The hydrolysis gave better results after increasing the reaction time to 5.5 and decreasing the amount of PLA to 1 g, but keeping the ratios. However, the AIL decomposed which interfered with the titration to determine the conversion. So, a second mixture was introduced with only water and AIL and the result of the titration of this mixture was used as a correction. After the correction the reaction with a mass ratio of 6:1:0.5, a temperature of 130 °C and a reaction time of 5.5 hours, a conversion of 95.56% was obtained.

The experiment was then repeated with these latter conditions, but with the synthesized 2-hydroxyethyl ammonium acetate as catalyst. The hydrolysis gave a conversion of 97.71%, which is better than the best result reported in the literature (93.93% for the AIL [Bmim][OAc]). However, the reaction time in this work was longer, which made it difficult to determine which of the to ionic liquids would be the best for the hydrolysis. The result obtained for 2-hydroxyethyl ammonium acetate was slightly better than the result obtained for [Emim][OAc] in this work (95.56%). Both ionic liquids might have similar conversion, but it is advised to used the protic ionic liquid, since these are greener than AILs and have a lower production cost.

To conclude, the proper method of synthesis for the PILs and DES might be found, but there is still research required to actually confirm their effectiveness in the applications.

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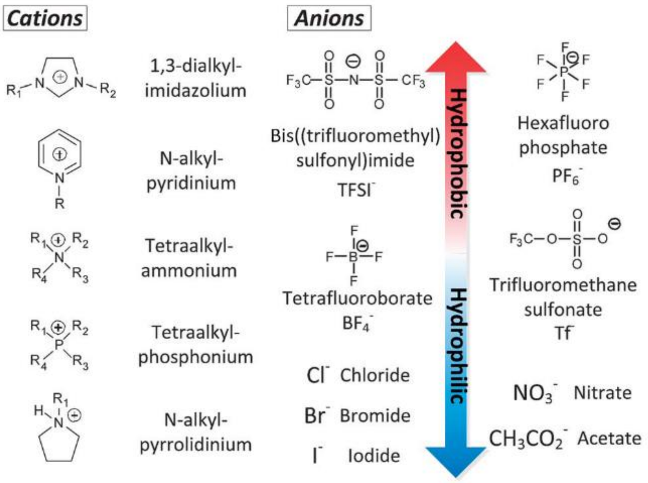
Extended Abstract

***Abstract* De interesse voor protische ionische vloeistoffen en diep eutectische oplosmiddelen is de afgelopen jaren toegenomen. Dit is een direct gevolg van de zoektocht naar groenere, niet-vluchtige alternatieven voor vluchtige organische oplosmiddelen. Het doel van dit werk was om een reeks op alkanolamine gebaseerde protische ionische vloeistoffen en een op menthol gebaseerd diep eutectisch oplosmiddel te synthetiseren voor toepassingen die in laboratoria en de industrie kunnen worden gebruikt. Deze toepassingen omvatten het gebruik bij de voorbehandeling van biomassa om de cellulose toegankelijker te maken voor enzymatische reacties, als katalysator bij de hydrolyse van polymelkzuur en als oplosmiddel bij de vloeistof-vloeistof extractie van waterige alcoholmengsels. Om dit doel te bereiken, werd de meest geschikte synthesemethode gekozen door verschillende in de literatuur gerapporteerde en toegepaste methoden te vergelijken. De gesynthetiseerde oplosmiddelen werden gekarakteriseerd om de synthesemethode te bevestigen. Voor de protisch ionische vloeistof 2-hydroxyethylammoniumacetaat (2-HEAA) en het diep eutectische oplosmiddel L-menthol:decaanzuur bevestigde de karakterisering dat de synthese inderdaad succesvol was. De brekingsindex en de dichtheid van 2-HEAA waren respectievelijk 1,47009 ± 0,00006 bij 25 ° C en 1,154844 ± 0,000023 g / cm3 bij 20 ° C. Tenslotte werd het gesynthetiseerde 2-HEAA getest bij de hydrolyse van poly (melkzuur).**

***Keywords* Protisch ionische vloeistoffen; Alkanolamines; Diep eutectisch solvent; Menthol; Polymelkzuur; Hydrolyse**

I. INTRODUCTIE

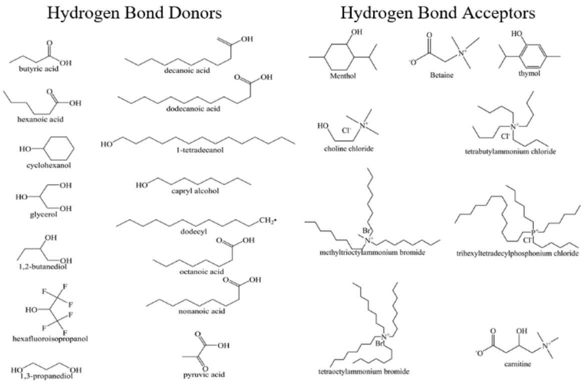
Er is de afgelopen jaren veel onderzoek gedaan naar het vinden van groenere alternatieven voor vluchtige organische oplosmiddelen (VOS). Een van deze alternatieven die veel aandacht heeft gekregen is de groep van de ionische vloeistoffen. Ionische vloeistoffen (ILs) zijn zouten die zich in vloeibare toestand bevinden bij temperaturen onder 100 ° C. Deze groep wordt beschouwd als een veelbelovend alternatief, voornamelijk vanwege hun lage dampspanning, maar ook vanwege hun onbrandbaarheid en hun chemische en thermische stabiliteit. Een van de meest opvallende feiten over deze oplosmiddelen is dat hun eigenschappen kunnen worden afgestemd op specifieke toepassingen door het kation en / of anion te veranderen [1], [2]. De meest gebruikte kationen en enkele van de mogelijke anionen die ermee gecombineerd kunnen worden om ILs te vormen, worden gegeven in Figuur 1, samen met hun hydrofoob karakter.



Figuur 6: Structuren van de meest gebruikte kationen en anion dat met deze kunnen gecombineerd worden.

Alhoewel ionische vloeistoffen kunnen beschouwd worden als ‘groene’ alternatieven, zijn er nog enkele nadelen waardoor ze geen ideale alternatieven zijn. Deze nadelen zijn de volgende: de hoge bijbehorende kosten, de vereiste hoge mate van zuiverheid en een toxiciteit en biologische afbreekbaarheid dat nog niet zijn vastgesteld.

Onlangs is de aandacht verschoven naar diep eutectische oplosmiddelen (DES's). Deze oplosmiddelen zijn mengsels van een of meer waterstofbruggen (HBD's) en een of meer waterstofbruggen (HBA's) bij de eutectische samenstelling. Ze hebben dezelfde gunstige eigenschappen als de ionische vloeistoffen, maar DES's elimineren deze nadelen omdat de meeste DES's zijn samengesteld uit verbindingen die zijn verkregen uit hernieuwbare bronnen [3]. Deze meest gebruikte HBD's en HBA's voor de synthese van diep eutectische oplosmiddelen worden getoond in Figuur 2.



Figuur 7: Meest gebruikte waterstofbrugdonoren (links) en meest gebruikte waterstofbrugacceptoren (rechts)

In deze context is het belangrijkste doel van deze werk is het produceren en karakteriseren van op alkanolamine gebaseerde protische ionische vloeistoffen (PILs) en een op L-menthol gebaseerde DES voor toepassingen zoals: het gebruik bij de voorbehandeling van biomassa, als katalysator bij de hydrolyse van polymelkzuur en als extractiemiddel voor de vloeistof-vloeistof extractie van waterige alcoholmengsels.

II. MATERIALEN EN METHODEN

Verschillende synthesemethoden in de literatuur werden met elkaar vergeleken om de meest geschikte methode te vinden om de gewenste oplosmiddelen te synthetiseren en op te zuiveren. De meest geschikte werden vervolgens aangepast.

A. 2-hydroxyethylammoniumacetaat

Voor het PIL 2-hydroxyethylammoniumacetaat (2-HEAA) was de meest efficiënte synthesemethode de neutralisatiereactie van 2-hydroxyethylamine (Sigma-Aldrich, ≥ 99,5%) met azijnzuur (Sigma-Aldrich, ≥ 99%). Het 2-hydroxyethylamine werd eerst in een drienekkolf met ronde bodem geladen. De kolf wordt vervolgens gemonteerd in een thermostatisch bad (RTE-200; Neslab) voor koeling, dat op 20 ° C wordt gehouden om kristallisatie van de PIL te voorkomen. De kolf wordt dan uitgerust met een refluxcondensor om de reagentia in de gasfase te condenseren. De reactie wordt gestart door druppelsgewijs een kleine overmaat van het zuur toe te voegen om volledige conversie te verzekeren van het 2-hydroxyethylamine. Na de toevoeging wordt het mengsel een 24 uur bij 20 ° C geroerd om een zo volledig mogelijke conversie te verzekeren. De voortgang van de reactie werd gevolgd met een refractometer (Abbemat; Anton Paar) en werd als voltooid beschouwd wanneer de brekingsindex de waarden in de literatuur benaderde en wanneer er geen vaste stoffen of kristallen in de ionische vloeistof waren. De zuivering werd uitgevoerd door vacuümdrogen bij 100 ° C gedurende 6 tot 8 uur met meesleuren met methanol na 4 uur en 6 uur om de efficiëntie van de zuivering te verhogen.

B. Bis-(2-hydroxyethyl)ammoniumacetaat en Tris-(2-hydroxyethyl)ammoniumacetaat

De meest efficiënte synthesemethode voor bis- (2-hydroxyethyl) ammoniumacetaat (BHEAA) en voor tris- (2-hydroxyethyl) ammoniumacetaat (THEAA) is vergelijkbaar met die van 2-HEAA, maar met de neutralisatie van bis - (2-hydroxyethyl) amine en tris-(2-hydroxyethyl) amine met een lichte overmaat azijnzuur om een zo volledig mogelijke conversie te verzekeren. Het enige andere verschil is de temperatuur van het thermostatische bad. Dit is 30 ° C voor BHEAA en 25 ° C voor THEAA om te voorkomen dat de ionische vloeistof kristalliseert. De zuivering wordt uitgevoerd op dezelfde manier als beschreven voor 2-HEAA.

C. L-menthol:decaanzuur DES

De meest geschikte methode voor de synthese van de L-menthol: decaanzuur DES is door L-menthol (Sigma-Aldrich, ≥99%) en decaanzuur (Sigma-Aldrich, ≥98%) te mengen in een molverhouding van 65:35 en vervolgens het mengsel verwarmen totdat een homogene vloeistof wordt verkregen zoals *Martins et al.(2018)* [4] suggereert. Door een fout werd echter een verkeerde molverhouding van 35:65 gebruikt. De temperatuur werd vervolgens geleidelijk verhoogd van 40 ° C in stappen van 2 ° C tot 50 ° C. Toen beide verbindingen eenmaal in vloeibare toestand waren, werd een magnetische roerder aan het mengsel toegevoegd en het werd geroerd bij 260 tpm totdat een homogene vloeistof werd verkregen. Daarna zou de DES gezuiverd worden door vacuümdrogen gedurende 2 dagen bij een temperatuur van 60 ° C, zoals voorgesteld door *Verma et al. (2018)* [5].

III. RESULTATEN EN DISCUSSIE

A. Thermo-fysische eigenscappen van 2-HEAA

De brekingsindex (RI) (nD) van 2-HEAA bij 25 ° C en de dichtheid (ρ) bij 20 ° C werden vergeleken met de literatuur. De brekingsindex van 2-HEAA was 1,47009 ± 0,00006 en de dichtheid was 1,54844 ± 0,0000223 g/cm^3. Dit is te zien in respectievelijk Tabel 1 en Tabel 2. De literatuur-RI-waarde die het dichtst bij de gemeten waarden ligt, werd gerapporteerd door *Greaves et al. (2006)* bij 25 ° C (1.469 ± 0.0005) [6] en de literatuurdichtheid die het dichtst bij de gemeten dichtheden ligt, wordt gerapporteerd door *Hosseini et al. (2019)* bij 20 ° C (1.559 ± 0.000021 g/cm^3) [7].

De gemeten waarden lieten geen significante verschillen tussen elkaar zien. The measured values showed to be similar to some of the values mentioned in the literature. When comparing the literature values with each other they also showed large differences.

De gemeten waarden vertoonden gelijkenissen met sommige van de waarden uit de literatuur. De waarden uit de literatuur vertoonde grote verschillen met elkaar als ze met elkaar werden vergeleken zoals te zien is voor de dichtheid in Tabel 2 en in Tabel 1 voor de brekingsindex. Vanwege dit feit is het niet mogelijk om te concluderen dat de synthese succesvol was op basis van de thermofysische eigenschappen alleen, maar de gemeten waarden kunnen nog steeds als betrouwbaar worden beschouwd. De FT-IR en de NMR-spectra kunnen worden gebruikt om te bepalen of de synthese succesvol was zonder een foutmarge.

Tabel 3: Vergelijking van de gemeten en literaire brekingsindexen van 2-HEAA

$n_{D,\text{ dit werk}}$	$n_{D,\text{ literatuur}}$	Bron
1.47008	1.143682*	[8]
1.46997	1.4711*	[7]
1.47000	1.4754	[9]
1.47007	1.469	[6]
1.47010	-	-
1.47008	-	-

*: these values were measured at 20 °C.

Tabel 4: Vergelijking van de gemeten en literaire dichtheden van 2-HEAA

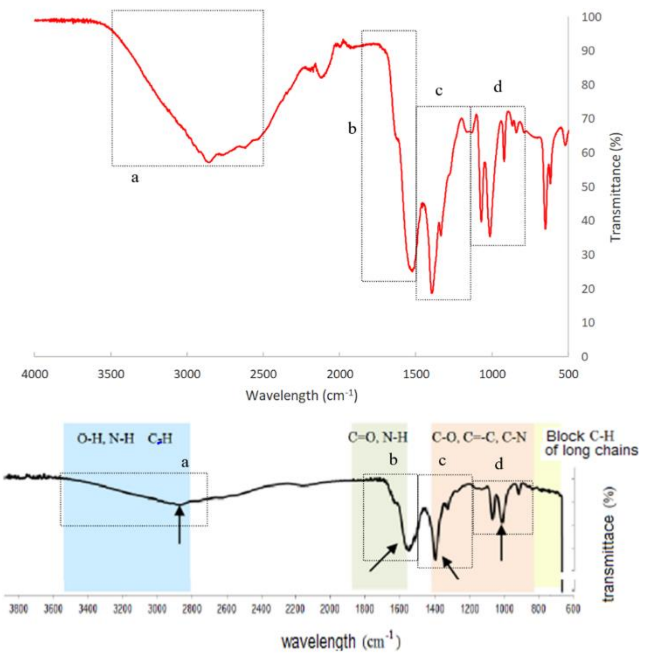
$\rho_{\text{dit werk}}$	$\rho_{\text{literatuur}}$	Bron
1.155057	1.151	[10]
1.154872	1.1559	[7]
1.154602	1.14866	[11]

B. *Karakterisatie van de solventen*

Na de synthese werd de synthesemethode van de oplosmiddelen gecontroleerd door hun karakterisering. Dit werd gedaan voor 2-HEAA door de FT-IR-, H-NMR- en C-NMR-spectra ervan op te nemen en voor de DES door een van de eigenschappen ervan te controleren.

1) *FT-IR spectrum van 2-HEAA*

Het FT-IR spectrum opgenomen in deze studie was vergelijkbaar met hetgene dat was opgenomen in het werk van *Rocha et al. (2017)* [9]. Beide spectra zijn te zien in Figure 3.



Figuur 8: 2-HEAA FT-IR opgenomen in dit werk (bovenste) en door *Rocha et al. (2017)* (onderste).

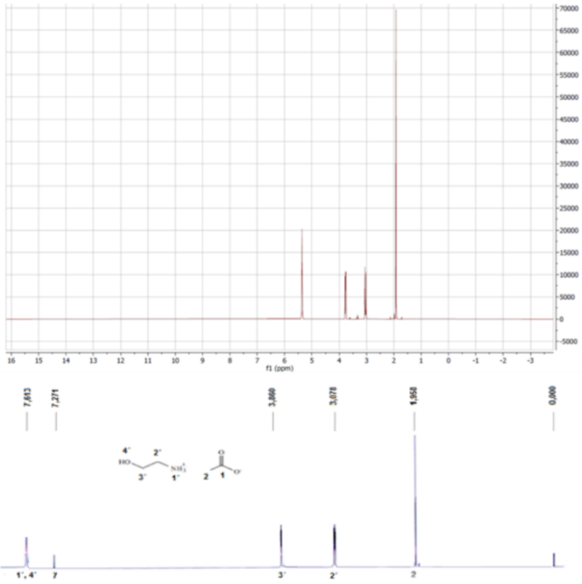
Beide spectra vertoonden een brede band in het bereik van 3500 tot 2500 cm^{-1} (a), wat kenmerkend is voor aminestructuren. De strektrillingen van hydroxyl, methyl en methyleen zijn ook in deze band opgenomen. De band tussen 1800 en 1500 cm^{-1} wordt beschouwd als een gecombineerde band van de C =O-strek- en N-H-krommingstrillingen.

De banden tussen 1500 en 800 cm^{-1} worden veroorzaakt door de C-O- en de C-N-bindingen. De band van 1500 tot 1200 cm^{-1} is het resultaat van de C-O strektrillingen en de band van 1200 tot 800 cm^{-1} is het resultaat van de C-N strektrillingen.

De enige band die de aanwezigheid van een soort onzuiverheid kan aangeven, is die tussen 800 - 500 cm^{-1}. Deze onzuiverheid is dan hoogstwaarschijnlijk een verbinding met een niet-gesubstitueerde cis-dubbele binding (800 - 680 cm^{-1}) of een enkelvoudig gesubstitueerde aromatische verbinding (680 cm^{-1} en op ± 750 cm^{-1}). De H- en C-NMR kunnen meer informatie geven over deze mogelijke onzuiverheden. Naast deze ene band vertonen de spectra een significante gelijkenis die aangeeft dat de synthese succesvol was.

2) *H-NMR spectrum van 2-HEAA*

Het H-NMR spectrum opgenomen in dit werk, is net zoals het FT-IR spectrum, vergelijkbaar met het spectrum opgenomen door *Rocha et al. (2017)* [9]. Beide spectra zijn gegeven in Figure 4.



Figuur 9: 2-HEAA H-NMR spectra opgenomen in dit werk (bovenste) en door *Rocha et al. (2017)* (onderste).

De eerste piek (vanaf rechts) bij δ = ± 2 ppm wordt hoogstwaarschijnlijk veroorzaakt door de waterstofatomen in de methylgroepen. De volgende pieken bij δ = 3 ppm en δ = 3.8 ppm zijn hoogstwaarschijnlijk het resultaat van de waterstofatomen in de methyleengroepen respectievelijk naast de ammoniumgroep en de hydroxylgroep.

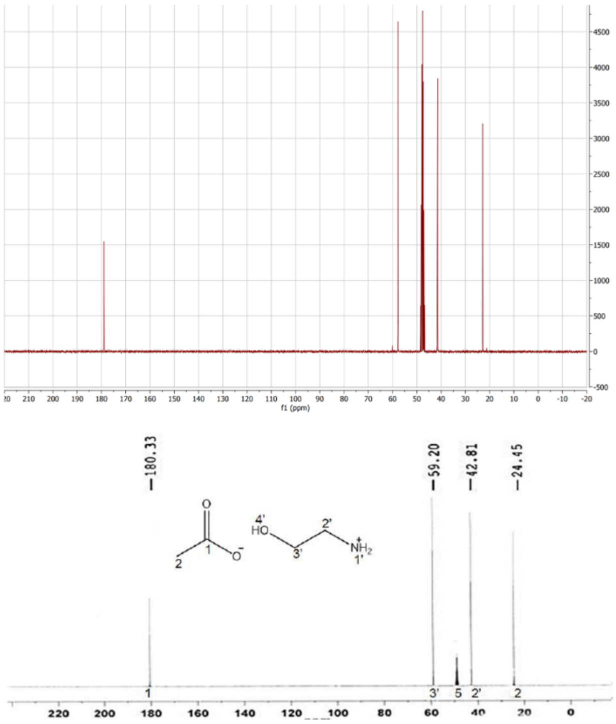
De andere toppen van beide spectra zijn verschillend. In het spectrum dat in dit werk wordt geregistreerd, wordt de piek op δ = ± 5,4 ppm hoogstwaarschijnlijk veroorzaakt door de waterstof in de hydroxylgroepen. Normaal gesproken zou deze piek rond δ = 0,5 ppm verschijnen, maar de waterstof wordt sterk afgeschermd door de vorming van waterstofbruggen met het oplosmiddel gedeutereerde methanol.

De pieken in het spectrum van Rocha et al. bij δ = 7,2 ppm en δ = 7,6 ppm worden waarschijnlijk veroorzaakt door het oplosmiddel dat wordt gebruikt voor de registratie van het H-NMR-spectrum, in dit geval gedeutereerde chloroform.

Het geregistreerde spectrum vertoont behalve de pieken van het oplosmiddel en de 2-HEAA geen andere pieken. Dit leidt tot de veronderstelling dat de synthese succesvol was.

3) C-NMR spectrum van 2-HEAA

Het in dit werk geregistreerde C-NMR-spectrum is hetzelfde als het spectrum dat is vastgelegd door *Rocha et al. (2017)* [9], wat werd verwacht aangezien beide spectra voor dezelfde component in hetzelfde oplosmiddel (gedeutereerde methanol) werden geregistreerd. Beide spectra zijn weergegeven in Figuur 5.



Figuur 10: 2-HEAA C-NMR spectra opgenomen in dit werk (bovenste) en door *Rocha et al. (2017)* (onderste).

De eerste piek (vanaf rechts) wordt veroorzaakt door de koolstof in de methylgroep op het acetaation. De volgende piek is het resultaat van de koolstof uit de methyleengroep naast de ammoniumgroep. De volgende piek is het resultaat van de koolstof in de gedeutereerde methanol. De laatste twee pieken worden veroorzaakt door respectievelijk de koolstof in de methyleengroep naast de hydroxylgroep en de koolstof in de carboxylgroep.

Er zijn geen andere pieken aanwezig dan de pieken veroorzaakt door 2-HEAA en de oplosmiddelen. Dit leidt tot de conclusie dat er geen significante onzuiverheden aanwezig zijn, dus de synthesemethode kan als succesvol worden beschouwd.

4) L-menthol:decaanzuur DES

De synthese van het L-menthol: decaanzuur DES wordt gecontroleerd door een van zijn eigenschappen te testen. De gekozen eigenschap is de onmengbaarheid met water omdat het doel is om het als oplosmiddel toe te passen bij de extractie van waterige alcoholmengsels en aangezien er maar een paar DES's zijn die deze eigenschap bezitten.

Na het mengen van een kleine hoeveelheid DES met water bleek deze eigenschap in feite te bezitten. Het feit dat de DES samen met deze eigenschap bij kamertemperatuur vloeibaar was, geeft een goede indicatie dat de synthese zelf succesvol was en dat in de toekomstige synthese alleen de juiste molverhouding moet worden gebruikt.

IV. HYDROLYSE VAN PLA

Een van de aprotische ionische vloeistoffen (AIL's) ([Emim] [OAc]) beschreven door *Song et al.(2014)* [12] werd getest als katalysator bij de hydrolyse van PLA. De voorwaarden zijn beschreven in *McKeown et al. (2020)* [13]: een massaverhouding van 12: 2: 1 (water: PLA: IL), een temperatuur van 130 ° C en een reactietijd van 2 uur. Er werd een conversie van ongeveer 90,86% verwacht, maar na de reactie was nog ongeveer een derde van de oorspronkelijke PLA over, wat aangeeft dat deze conversie niet wordt bereikt. De resultaten na het veranderen van de reactietijd naar 5,5 uur en de hoeveelheid PLA tot 1 g waren veel beter. Tijdens dit experiment werden alle andere voorwaarden en de verhoudingen hetzelfde gehouden. Het grootste probleem is nu dat tijdens dit experiment de ionische vloeistof ook ontleedde, wat de titratie die werd gebruikt om de hoeveelheid melkzuur te bepalen, verstoorde. Na dit experiment werden er altijd twee *pressure tubes* gemaakt: één met water, PLA en IL in de massaverhouding van 6: 1: 0,5 en één met alleen water en IL in de massaverhouding van 6: 1. Deze laatste werd getitreerd en gebruikt als correctie voor de afbraak van de ionische vloeistof. In het experiment werd onder de volgende omstandigheden een conversie van 95,56% bereikt: een massaverhouding van 6: 1: 0,5 (water: PLA: IL), een temperatuur van 130 ° C en een reactietijd van 5,5 uur.

De hydrolyse werd uitgevoerd met een massaverhouding van 6: 1: 0,5 (water: PLA: IL), een temperatuur van 130 ° C en een reactietijd van 5,5 uur, maar dit keer met het gesynthetiseerde PIL 2-HEAA. Met deze PIL werd een conversie van 97,71% behaald, wat beter was dan het beste resultaat behaald door Song et al. [12]. Dit resultaat werd verkregen voor de AIL [Bmim] [OAc] bij een massaverhouding van 12: 2: 1 (water: PLA: IL), een temperatuur van 130 ° C en een reactietijd van 2 uur en had een waarde van 93,93 %. Het resultaat dat bij dit werk wordt verkregen is beter, maar er moet worden opgemerkt dat de reactietijd veel korter was. Als de reactietijd hetzelfde was, had de hydrolyse [Bmim] [OAc] mogelijk een vergelijkbare of zelfs betere conversie opgeleverd.

De conversie verkregen voor 2-HEAA was iets beter dan de conversie verkregen voor de AIL [Emim] [OAc] in dit werk. Het wordt aangeraden om de PIL te gebruiken in plaats van de AIL, ook al hebben ze vergelijkbare conversies. Dit komt omdat PIL's een groener karakter hebben en lagere productiekosten hebben dan AIL's.

V. CONCLUSIE

Voor de toepassing van deze protische ionische vloeistoffen en diepe eutectische oplosmiddelen bij de voorbehandeling van biomassa, de hydrolyse van poly (melkzuur) of de vloeistof-vloeistof extractie van waterige alcoholmengsels, is het belangrijk om de juiste synthesemethode te gebruiken om de gewenste eigenschappen voor deze toepassingen.

De thermo-fysische eigenschappen (brekingsindex en dichtheid) waren vergelijkbaar met sommige van de waarden uit de literatuur, maar er waren grote verschillen tussen de literatuurwaarden onderling. Door deze grote verschillen is het niet mogelijk om alleen met de thermo-fysische eigenschappen de synthese succesvol te verklaren. De FT-IR en de NMR spectra kunnen gebruikt worden om te bepalen of de synthese succesvol was zonder een foutmarge.

De karakterisering van 2-hydroxyethylammoniumacetaat via FT-IR, H-NMR en C-NMR toonde aan dat de synthesemethode die in dit werk wordt gebruikt de juiste is. De onmengbaarheid van het diepe eutectische oplosmiddel met water en het feit dat het vloeibaar was bij kamertemperatuur, gaf een goede indicatie dat de synthese zelf succesvol was. Dit betekent dat de synthesemethode de juiste zou zijn als de juiste mengverhouding van L-methol: decaanzuur wordt gebruikt.

Het testen van de hydrolyse van poly (melkzuur) met de beschreven AIL [Emim] [OAc] als katalysator bij een massaverhouding van 12: 2: 1 (water: PLA: IL), een temperatuur van 130 ° C en een reactie tijd van 2 uur leverde niet de verwachte conversie van 90,86% op. De hydrolyse gaf betere resultaten na het verhogen van de reactietijd tot 5,5 en het verlagen van de hoeveelheid PLA tot 1 g, maar met behoud van de verhoudingen. De AIL ontbond echter, wat de titratie verstoorde om de conversie te bepalen. Er werd dus een tweede mengsel geïntroduceerd met alleen water en AIL en het resultaat van de titratie van dit mengsel werd gebruikt als correctie. Na correctie van de reactie met een massaverhouding van 6: 1: 0,5, een temperatuur van 130 ° C en een reactietijd van 5,5 uur werd een conversie van 95,56% verkregen.

Het experiment werd vervolgens herhaald met deze laatste omstandigheden, maar met het gesynthetiseerde 2-hydroxyethylammoniumacetaat als katalysator. De hydrolyse gaf een conversie van 97,71%, wat beter is dan het beste resultaat vermeld in de literatuur (93,93% voor de AIL [Bmim] [OAc]). De reactietijd bij dit werk was echter langer, wat het moeilijk maakte om te bepalen welke van de ionogene vloeistoffen het beste zouden zijn voor de hydrolyse.
Het resultaat verkregen voor 2-hydroxyethylammoniumacetaat was iets beter dan het

resultaat verkregen voor [Emim] [OAc] in dit werk (95,56%). Beide ionische vloeistoffen kunnen een vergelijkbare conversie hebben, maar het wordt aangeraden om de protische ionische vloeistof te gebruiken, omdat deze groener zijn dan AIL's en lagere productiekosten hebben.

Concluderend kan de juiste synthesemethode voor de PIL's en DES worden gevonden, maar er is nog steeds onderzoek nodig om hun effectiviteit in de toepassingen daadwerkelijk te bevestigen.

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List of Abbreviations and Symbols

Abbreviations

VOCs	Volatile Organic solvents/Compounds
ILs	Ionic Liquids
DES	Deep Eutectic Solvents
HBD	Hydrogen Bond Donor
HBA	Hydrogen Bond Acceptor
AILs	Aprotic Ionic Liquids
PILs	Protic Ionic Liquids
HA	Brønsted acid
B	Brønsted base
TFSI	bis(trifluoromethane) sulfonimide
BETI	bis(perfluoroethyl) sulfonimide
CILs	Chiral Ionic Liquids
SPS	Switchable-Polarity Solvents
ChCl	Cholinium Chloride
RTILs	Room-Temperature Ionic Liquids
PGSE-NMR	Pulse-field-Gradient Spin Echo NMR
EAA	Ethyl Ammonium Acetate
EAN	Ethyl Ammonium Nitrate
PAN	Propyl Ammonium Nitrate
PEMFC	Polymer Electrolyte Membrane Fuel Cells
PLA	Poly (Lactic Acid)
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
REACH	Registration, Evaluation, Authorization and registration of Chemicals
$scCO_2$	Super Critical CO_2
AC	Activated Carbon
2-HEAA	2-HydroxyEthyl Ammonium Acetate
BHEAA	Bis-(2-HydroxyEthyl) Ammonium Acetate
THEAA	Tris-(2-HydroxyEthyl) Ammonium Acetate
ETSE	Escuela Technica Superior de Ingenieria
BEA	Bis-(2-HydroxyEthyl)amine
TEA	Tris-(2-HydroxyEthyl)amine
DA	Decanoic Acid
PC-SAFT	Pertubed Chain-Statistical Associating Fluid Theory
AA	Acetic Acid
2-HEA	2-HydroxyEthyl Amine
KF	Karl-Fischer
2-HEA	2-hydroxyethylamine
FTIR	Fourier-Transform Infra-Red
RI	Refractive index
SDG	Sustainable Development Goal

Symbols

ΔpKa^{aq}	Difference between the pKa^{aq} value of the constituent acid and protonated base
pKa^{aq}	Negative base -10 logarithm of the acid dissociation constant
K_{eq}	Equilibrium constant
k_f	Forward rate of the equilibrium reaction
k_r	reverse rate of the equilibrium reaction
T_g	Glass transition temperature
T_m	Melting point
T_d	Decomposition point
T_b	Boiling point
ρ	Density
n_D	Reftractive index
N	Number of ions per unit of volume
α	polarizability
μ	Viscosity
Λ	Molar conductivity
ϕ	Fluidity
Λ_{imp}	Molar conductivity obtained by dividing the ionic conductivity by the molar concentration
Λ_{NMR}	Molar conductivity obtained via PGSE-NMR
T	Absolute temperature in K
D_{cation}	Diffusion coefficient of the cation
D_{anion}	Diffusion coefficient of the anion
P_{vap}	vapor pressure
$\Delta_{vap}H$	evaporation enthalpy
τ	Oscillation period of the U-tube in the density meter
w_1	Weight of the filtrate obtained after filtering the mixture obtained after the hydrolysis of PLA
w_2	Weight of a small amount taken from the liquid associated with w_1
C	Concentration of the NaOH used in the titration of w_2
V	Volume of the NaOH used in the titration of w_2
w_3	Theoretical weight of the lactic acid in w_2
s	Standard deviation
x_i	Measured value
$\bar{x}$	Mean
n	Number of measurements
x	Value that is a possible outlier
$\bar{x}^*$	Mean of the measurements without the outlier
s^*	Standard deviation of the measurements without the outlier

1. Literature study

1.1. Introduction

Traditional volatile organic compounds (VOCs) have many industrial applications like media for different types of reactions, extraction fluid, etc. VOC usually are relatively small molecules that have weak intermolecular forces between them. These properties make these VOC highly volatile. This is a problem because these solvents are also flammable and most of them are also toxic, which makes them not only an environmental hazard but also a safety hazard. This is the reason why in context of sustainability there has been much interest in finding a non-volatile alternative for these VOC. Very promising candidates for their replacement are ionic liquids because they have a low vapor pressure making them non-volatile, which makes operations with these liquids safer and environmentally more acceptable [1]. Some of the advantages of ionic liquid over VOCs are summarized in Table 5.

Table 5: Advantages of ionic liquids over VOCs [1]

Property	Ionic liquids	VOCs
Volatility	Low to non-existent	high
Chemical stability	high	low
Flammable	Non-flammable	inflammable
Toxicity	Not yet ascertained	high
Thermal stability	high	low

Ionic liquids (ILs) are fused salts that are in a liquid state at temperatures below 100 °C. These substances have interesting physical and chemical properties. Some of these properties are a negligible or low vapor pressure, wide liquid-range, unique permittivity, high electrical conductivity, and the ability to dissolve both polar and non-polar organic or inorganic substances, high thermal stability and a wide electrochemical window. This is not the most notable thing about the ionic liquids. The most notable fact about these ILs is that the properties can be tailored by appropriately combining different cations and/or anions. This further increase their applicability in industrial applications [1]–[3].

Even though ionic liquids a good alternative for the traditional VOC, there are still some disadvantages that make them not ideal. The disadvantages are the production cost, the uncertainty about their toxicity, the necessity for high purity and their poor biodegradability, which give ionic liquids a negative life cycle assessment. Deep eutectic solvents (DES) were developed to resolve these issues. Deep eutectic solvents (DES) are mixtures of one or more hydrogen bond donors (HBD), such as amines, carboxylic acids, alcohols and carbohydrates, and one or more hydrogen bond acceptors (HBA), such as quaternary ammonium salts, which can self-associate through hydrogen-bonding [4]. The HBD acts as a complexing agent and increases the effective size of the HBA, which decreases the interactions with the HBD, resulting in a decreased freezing point of the mixture. DES have similar beneficial properties as ILs while eliminating the disadvantages of ILs [5].

1.2. Aims of this work

The main goal of this work is to synthesize and characterize ionic liquids and a deep eutectic solvent for the use in the pretreatment of biomass, as catalyst in the hydrolysis of poly (lactic acid) and as solvent in the liquid-liquid extraction of aqueous mixtures of alcohols. For this purpose, protic ionic liquids based on alkanolamines and acetic acid and a L-menthol- and decanoic acid-based deep eutectic solvent were produced. The alkanolamines used in this study are hydroxyethyl amine, bis-(hydroxyethyl)amine and tris-(hydroxyethyl)amine.

First, the current state-of-the-art has been analyzed and discussed. The characterization of the synthesized solvents was done in three ways: via Fourier-transform infra-red spectroscopy, H-NMR and C-NMR. The thermophysical properties, refractive index, density, and the refractive index were also studied. Additionally, a comparison was made between the characterization and the thermophysical properties in this study and in the literature. Finally, the produced solvents were tested as catalyst in the hydrolysis of poly (lactic acid).

1.3. Different categories of ionic liquids

Ionic liquids can be divided into two main categories: aprotic ionic liquids (AILs) and protic ionic liquids (PILs). Beside these two categories, there are also a bunch of smaller groups of ionic liquids. These some of these categories of ionic liquids will be discussed. A short introduction is given hereby to each category.

1.3.1. Aprotic ionic liquids

Aprotic ionic liquids are also called “classic”, “conventional” or “traditional” ionic liquids. Bulky cations, such as pyridinium and imidazolium ions, have been proven to be appropriate starting points for these ionic liquids (Figure 11). These cations are combined with a large variety of anions [6]. One of the reactions to produce these aprotic ionic liquids is a metathesis reaction, which usually require a catalyst [1]. Another production reaction is the one that transfers an alkyl group to the basic nitrogen site through S_N2 reaction [7]. The alkylation reaction is illustrated for 1-methylimidazole and a butyl halide with acetonitrile as catalyst in Figure 12. The metathesis reaction is illustrated for 1-butyl-3-methylimidazolium chloride and a potassium salt in Figure 13.

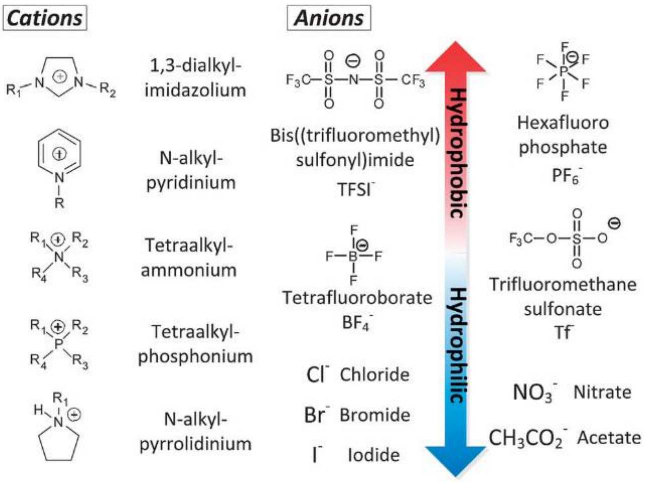

Figure 11: Structures of most commonly used cations and anions that can be combined to form ionic liquids [8]

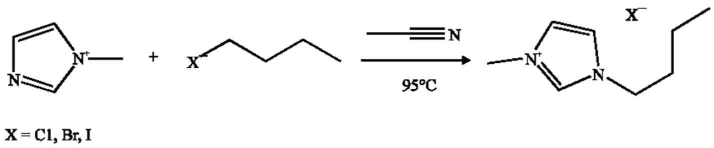

Figure 12: Alkylation of 1-methylimidazole with butyl halide [9]

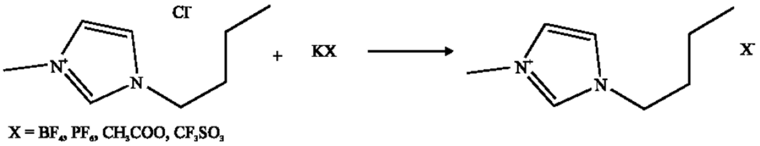

Figure 13: Metathesis of 1-butyl-3-methylimidazolium chloride with a potassium salt [9]

It must be mentioned that these ionic liquids are not in an ionic form in solution. They are pure compounds that are conceptually similar to regular salt (NaCl) that is in a liquid state. The big difference is that the Coulombic interactions between the cations and the anions are stronger in NaCl which leads to a higher melting point [1]. Another important difference is that in ILs molecular interactions, like hydrogen bonding, π- π stacking and other dispersive forces, are also present [7].

The ions in an ionic liquid are not spherical but each ion has its own shape and functionality. This leads to subtle changes in the physical properties due to dipole interactions, hydrogen-bonding and dispersive forces, but the Coulombic force is still the strongest force in ionic liquids. These above mentioned forces are weak enough to keep the IL liquid at ambient temperatures [1].

However, these types of ionic liquids have several disadvantages. The main disadvantages are their high production cost and necessity for a high purity, which make them somewhat impractical for industrial use. The presence of impurities can not only affect their physical and chemical properties, but also their catalytic activity and their electrochemical behavior. This means that it is very important to monitor the purity of the ionic liquids. Typical impurities are unreacted reagents, halide impurities that are formed as by-product in the metathesis, protic or other ionic impurities caused by an incomplete metathesis and water from the reagents or absorbed from the atmosphere [1], [10] .

1.3.2. Protic ionic liquids

One way of bypassing the high cost of AILs is using protic ionic liquids instead. Protic ionic liquids are formed by a proton transfer from a Brønsted acid (HA) to a Brønsted base (B).

$$HA + B \rightleftharpoons A^- + HB^+ \qquad [1]$$

This transfer from acid to base leads to the formation of both proton-donor and proton-acceptor sites, which eventually result in the key properties that distinguish these PILs from other ionic liquids except for the Brønsted ionic liquids. Brønsted ionic liquids can be both PILs or AILs depending on whether the available proton is located on the cation or the anion [10],[11].

Like mentioned earlier, it is the proton transfer that causes the distinguishing features between the PILs and the AILs. These features are a non-negligible vapor pressure and the availability of a proton for hydrogen bonding. Using stronger acids and/or bases increases the driving force behind this reaction, which results in an improved proton transfer. The ΔpKa^{aq} value of the ionic liquid can be considered an indication for how strongly the proton will be transferred. This is the difference between the pKa^{aq} value of the constituent acid and the protonated base in water. The downside of this consideration is that the *pKa* values are usually given for aqueous solutions, which means that this might not be appropriate for non-aqueous PILs [3],[10],[11]. The ΔpKa^{aq} value can be related to the equilibrium constant (K_{eq}) of the proton transfer via Equation 1:

$$K_{eq} = 10^{\Delta pKa^{aq}} \qquad (1)$$

A high equilibrium constant is desired, because this means that the equilibrium will completely shift to the right side, which indicates that the proton transfer between acid and base is complete. This can be achieved by choosing an acid and base with a ΔpKa^{aq} value high enough to ensure a full proton transfer.

Miran et al. (2018) found that a ΔpKa^{aq} higher than 10 was be required for the full proton transfer, but according to equilibrium calculations indicate a $\Delta pKa^{aq} = 4$ should be sufficient to obtain a proton transfer that is 99% complete. *Stoimenovski et al.(2010)* proved that a ΔpKa^{aq} of 4 is sufficient to obtain 99% proton transfer for primary amines. However, tertiary amines required a ΔpKa^{aq} of 6. *Stoimenovski et al.* (2010) also discovered there are secondary amines that required a ΔpKa^{aq} like the one for primary amines, but there are also secondary amines that required a ΔpKa^{aq} value similar to the one required for tertiary amines. In other words, the secondary amines seem to be transitional depending on the details of its chemical structure [12].

The molecular origins of these differences are likely related to the differences in the hydrogen bonding environments. In primary amines, the cation has multiple hydrogen bond donors available to interact with the anion. This solvation might even be considered similar to that of water. In contrast, the tertiary amines offer an environment, which is less stabilizing for the anion and thus proton transfer is energetically less favored. Another factor in the proton transfer is the possibility to form more complex species of the $A\text{-}H\text{-}A^-$ type. In tertiary systems, formation of these ions in mixtures which are acid rich, thus providing more hydrogen bond donors to assist the stabilization of A^-, was more beneficial for a complete proton transfer than stoichiometric mixtures [12].

Like mentioned earlier, in the ideal case the only remaining species that are present in the solution are the resulting cation and anion. This will not be the case in reality and there will always be some neutral base and acid species remaining and ion association to form neutral species is possible. This results in low ionic conductivities that are atypical for PILs. Therefore, it is important to be able to determine the ionicity of the ionic liquid together with its structure. The subject of ionicity is discussed in more detail in section 1.5.10 [10],[11].

Proton transfer is considered complete in a PIL with a high ΔpKa^{aq} value due to the high kinetics, since the ΔpKa^{aq} value can be linked to the kinetics via Equation 2:

$$10^{\Delta pKa^{aq}} = K_{eq} = \frac{k_f}{k_r} \ (2)$$

With k_f and k_r being the forward and the reverse rates of the equilibrium reaction [1]. However, in Brønsted acid-base mixtures with low ΔpKa^{aq} values still have a considerable amount of neutral reagents. The proton transfer is in these cases incomplete and these systems are for that reason not considered as true PILs, but rather as pseudo-PILs [3].

The association in protic ionic liquids was determined by *Greaves and Drummond (2008)* using Kohler's method. The disadvantage of this method is that both the viscosity and the density of the ionic liquid needs to be known. This study did not include any imidazolium protic ionic liquids. They showed that the tendency for aggregation is higher for primary ionic liquids than for tertiary ionic liquids. Primary alkylammonium PILs with a long chain length and which were produced with strong acids of bis(trifluoromethane)sulfonimide (TFSI) and bis(perfluoroethyl)sulfonimide (BETI) showed very little aggregation [11].

A result of this incomplete proton transfer is the vapor pressure of the ILs. The interaction energies between HB^+ and A^- are large, corresponding to the Coulomb force. On the other hand, the interactions between the HA and B neutral species are smaller, corresponding to the hydrogen bonding and van der Waals forces. This is the reason why PILs have a vapor pressure. This is important for their ability to be distillated which is discussed in section 1.10.1 [13].

1.3.3. Chiral ionic liquids (CILs)

Chiral compounds are molecules or ions with at least one stereocenter and which cannot be superposed on their mirror image, which is also called its enantiomer. Enantiomers have the same physical properties, except for their optical activities [14]. The source of chirality of the ILs can be provided by the cation and/or the anion (Figure 14). A large range of these CILs with chiral amino acid anions and ammonium, imidazolium and phosphonium cations have been prepared. This group of ILs is applied in asymmetric synthesis and in spectroscopic and chromatographic applications [7].

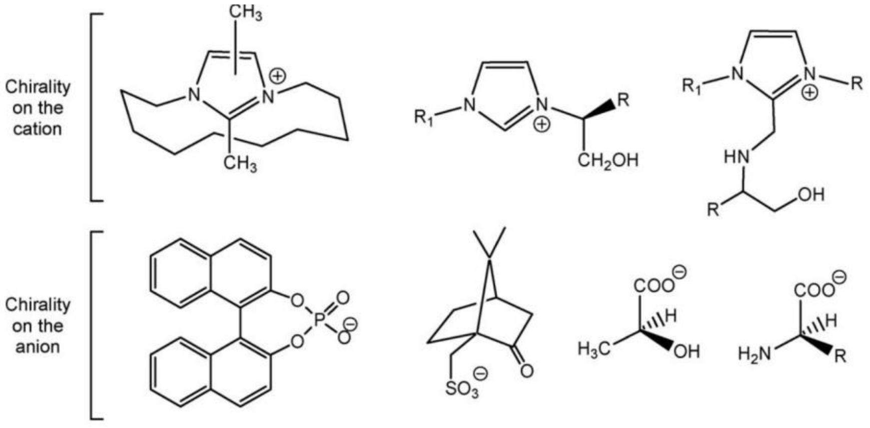

Figure 14: Examples of chiral anions and cations for the production of CILs [7]

1.3.4. Switchable-polarity solvents (SPS)

These solvents are neutral liquids that can be reversibly converted into ionic liquids by introducing CO_2. The mechanism behind switchable-polarity solvents is illustrated for a dialkylamine in Figure 15. The conversion back to the neutral liquid happens in the presence of N_2, argon gas or heat. These solvents have been utilized in post-reaction separation of products from homogeneous catalysts, which is discussed later in section 1.10.6 [7].

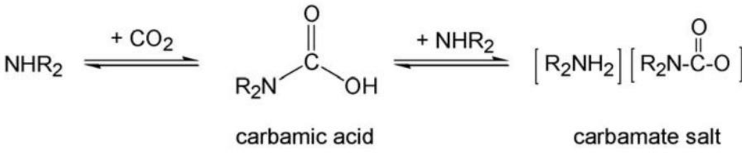

Figure 15: Mechanism behind SPS [7]

1.4. Deep eutectic solvent (DES)

Deep eutectic solvents (DES) are mixtures of one or more HBDs, such as amines, carboxylic acids, alcohols and carbohydrates, and one or more HBAs, such as quaternary ammonium salts, which can self-associate through hydrogen-bonding. The majority of the HBAs and the HBDs that are used to produce DES are gained from renewable resources and the most commonly used ones are given in Figure 16 [4]. The HBD acts as a complexing agent and increases the effective size of the HBA, which decreases the interactions with the HBD, resulting a decreased freezing point of the mixture. The point where the mixture shows a minimum freezing point is called the eutectic point (Figure 17). Some DES have no strict eutectic point, but they rather have glass transition temperature which is mostly close to the eutectic point. These mixtures are called low-melting mixtures or low-transition-temperature-mixtures.

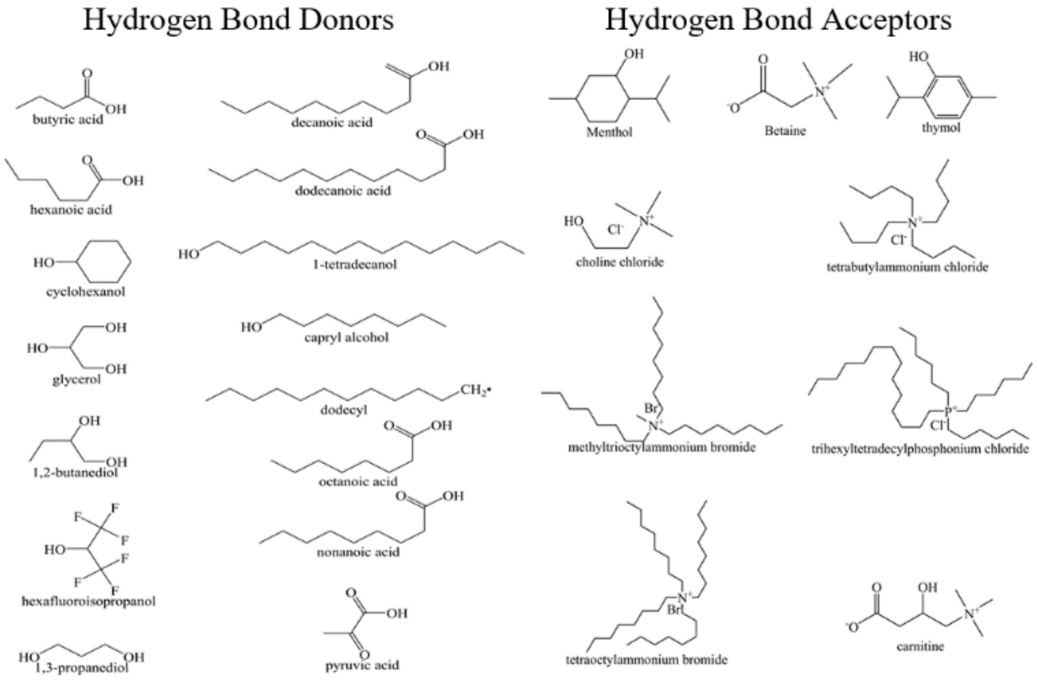

Figure 16: Most commonly used hydrogen bond donors (left) and hydrogen bond acceptors (right) for the synthesis of DES [15]

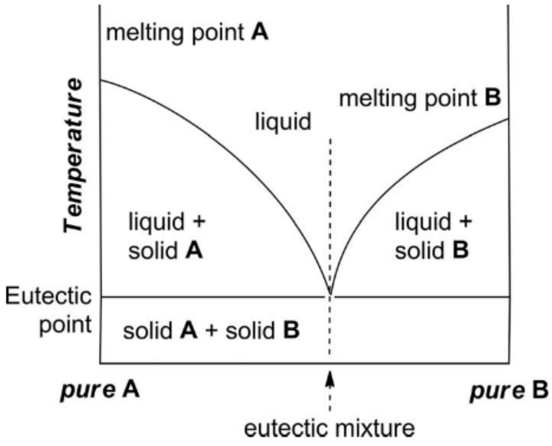

Figure 17: Phase diagram of a mixture of 2 components to illustrate the eutectic point [5]

The eutectic mixture is obtained by a one-step synthesis that involves mixing these components. The reagents are both solid at the beginning of the synthesis and at the end a eutectic mixture is obtained that is liquid at ambient temperatures, due to the decreased melting point. This property is related to the formation of intermolecular hydrogen bonds between the hydrogen bond donor and the hydrogen bond acceptor [16].

Like mentioned earlier, DES are appropriate replacements for ionic liquids, because of their similar physicochemical properties and, unlike traditional ILs, they are easy, simpler and cheaper to produce. This is a direct result of the one step synthesis which requires no prior purification of the reagents [16]–[18]. Besides this, most of them are biodegradable, biocompatible and non-toxic [19].

Deep eutectic solvents can be prepared using two methods: the heating method and the grinding method. The heating method is based on mixing of the two components and heating to elevated temperatures under continuous stirring until a homogeneous liquid is formed. In the grinding method, both components are mixed at ambient temperatures and then grinded in a mortar with a pestle until a homogeneous liquid is formed. The latter has been largely explored for the use of DES for pharmaceutical purposes [19]. Both preparation methods require no solvents and no by-products are generated, so no further purification is necessary.

The most popular DES are those based on the HBD cholinium chloride (ChCl) (Figure 18) because of their low cost, low toxicity, biodegradability and biocompatibility. ChCl can be extracted from biomass and is often regarded as a part of the vitamin B complex. It is readily available in bulk and it is produced with the highest possible atom economy, which means that all the initial components are part of the final product. Cholinium and other ammonium cations have been combined with various anions in order to find natural biocompatible and bio-renewable solvents [4], [6], [19].

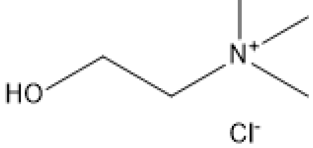

Figure 18: Structure of Cholinium Chloride

1.5. Properties of ILs

1.5.1. Toxicity and biodegradability

The low vapor pressure than that of the VOCs under normal conditions make the ILs a greener solvent, however this leads to the misconception that all 12 principles of green chemistry apply to these greener solvents. This leads to the believes that ILs also have a good biodegradability and a low toxicity. It should be noted that the majority of the precursors used to produce ionic liquids, like imidazole and pyridine with substituted alkyl groups ,are considerably toxic and environmentally hazardous. The trend in the toxicity of the ILs is that the longer the alkyl chain on either the cation or anion, the higher the toxicity of the IL. On the other side, it must also be mentioned that in principle ILs can be modified to be non-toxic [20],[21].

The toxicity is linked with the biodegradability of the ILs. ILs with a lower toxicity have a greater chance of undergoing biodegradation because they may be less toxic to the microorganisms that can break them down. Research by *Reid et al. (2017)* and *Oliveira et al. (2016)* showed that the biodegradability could also be linked to the length of the side chains of the cations, where cations with smaller side chains were more biodegradable and that the aprotic or protic nature did not matter to the biodegradability. However, *Oliveira et al. (2016)* proved that ILs with cations with side chains that contained less than four carbon atoms were not biodegradable at all [21], [22].

Some researchers are convinced that ILs can be designed to non-toxic and readily biodegradable. When comparing AILs and PILs, it was shown that the cation nature had a less pronounced effect compared to the effect of functionalized groups on the cation and variation in the anion only had a minor influence on their overall toxicity [22].

1.5.2. Glass transition temperature

For most applications it is desirable to work with liquids with a low viscosity and in some cases high conductivity is also desirable. These properties are often reflected in the glass transition temperature (T_g). The glass transition is indicative for the cohesive energy within the IL. This energy decreases due to repulsive Pauli forces that originate from the overlap of closed electron shells and this energy increases through Coulomb and van der Waals forces, since these forces work attractive. This means that the T_g can be decreased by decreasing the cohesive energy. This can be achieved by modification of the cation and/or the anion. [11].

It has been proven that decreasing the size of the cation or increasing its asymmetry also decreases the glass transition temperature. These modifications result in a lower cohesive energy and a bad packing of the cations and anions. The glass transition temperature for primary alkylammonium PILs can be slightly increased by increasing the chain length of the alkyl groups due to strong Van Der Waals interactions. The glass transition temperature can be drastically increased by adding a hydroxyl group on either the anion or the cation. This leads to more hydrogen bonding within the IL and works in favor of the cohesive energy between the species [3],[11].

1.5.3. Melting point

The melting point (T_m) of ILs can vary from below room temperature -these ILs are called room temperature ionic liquids (RTIL)-, to temperatures above 100 °C (protic molten salts). In general, the melting point can be reduced by decreasing the packing efficiency of the ions. The key factors are the same as for the decrease of the glass transition temperature: sufficient steric hinderance to decrease the packing efficiency and minimize the hydrogen bonding. On the one hand, *Greaves and Drummond (2008)* discovered that alkylammonium nitrate salts and 1-alkyl-2-alkylimidazolium salts with chloride or bromide anions had melting point above 100 °C. On the other hand, PILs which contained alkylammonium cations and small carboxylic anions or which had an imidazolium cation had melting points that approached those of RTILs [11].

1.5.4. Thermal stability

Most ionic liquids show a high thermal stability which is indicated by the decomposition temperature (T_d). The decomposition point or temperature is defined as the temperature at which a mass loss of 10 % is observed with thermogravimetric analysis [3]. This decomposition temperature is for most ILs above 350 °C. However, the long-term stability was often not described and in the few cases in which it was described, there was no identification of the decomposition products. The thermal stability is, just like the chemical stability of the ILs during catalytic reactions, dependent on the present impurities and the exposure to reactants, products and process conditions [7].

PILs have a boiling point (T_b) and a decomposition point (T_d), but for some PILs the decomposition occurs before they start boiling. Which of the two occurs first is depended on the proton-transfer energy. PILs with a large proton-transfer energy will decompose before they boil. Better thermal stabilities are observed for PILs which have anions that show little interaction with other ions and/or inorganic anions. It was found that PILs which contained carboxylate anions had lower thermal stability. This is due to the condensation reaction which forms amides. *Miran et al. (2018)* showed that the decomposition temperature increased linearly with increasing ΔpKa^{aq} value. They also proved that stronger hydrogen-bonding resulted in an easier dissociation back into the acid and the base, which in turn leads to a lower thermal stability [3],[11].

1.5.5. Density

Just like most of the properties, the density (ρ) is also dependent on the size and shape of the ions and on the ion-ion interactions. The density decreases slightly with increasing alkyl chains of alkylammonium cations, alkylimidazolium cations or alkylcarboxylate anions. This is valid for both protic and aprotic ILs. Among the PILs, the least dense ionic liquids were a combination of trialkylamines with long alkyl chains and with formic acid. This is a direct consequence of the bulkiness of this cation. Due to the high packing efficiency of primary amines, it is expected that they have higher densities than secondary amines, which are expected to have higher densities than tertiary amines. Heterocyclic amine cation containing ionic liquids had even higher densities than those of primary amines. Bases with an excess of hydrogen bond donors also increased the density of the resulting ionic liquid [10],[11].

1.5.6. Refractive index

The refractive index (n_D) of a material is an indication of its polarizability. The correlation of these two parameters is given by the Lorentz-Lorenz equation (Equation 3) [23].

$$\frac{{n_D}^2-1}{{n_D}^2+2} = \frac{4\pi}{3} * N * \alpha \qquad (3)$$

With N being the number of ions per unit of volume and α the mean polarizability. This equation shows that the polarizability increases with the refractive index. The alkylammonium ILs are the only ILs in the protic ionic liquid group of which the n_D-values are reported. The values for all alkylammonium ILs in *Greaves and Drummond (2008)* were around 1.5. This indicates that these PILs can be considered moderately polarizable. *Greaves and Drummond (2008)* also showed that an increase in the alkyl chain length resulted in a slight increase in the refractive index, while the substitution of a hydroxyl group on either the cation or anion causes a more drastic increase in the value of the refractive index [11].

1.5.7. Surface tension

Just like the refractive index, the alkylammonium ILs are the only ILs in the protic ionic liquid group of which the values of the surface tension are reported. Changes in anion or cation structure had the same effect on the surface tension of the ionic liquid. From this we can conclude that both the cation and the anion are present at the surface and affect the surface tension equally.

The model that is proposed for these alkylammonium ILs to investigate the effect of the structural changes on the surface tension assumes that the hydrocarbon chains are exposed to air while the charged groups are pointed towards the bulk. This implies that the surface tension increases with the chain length of the alkyl group, while branching on the alkyl chains decreases the surface tension. In general, the surface tension increases when the ions show a better packing efficiency or when the cohesiveness in the ionic liquid increase, for example by increasing the amount of hydrogen bonds. One way to increase the amount of hydrogen bonds is by substituting a hydroxyl group on either cation or anion [11].

1.5.8. Viscosity

Viscosity (μ) is highly dependent on the ion-ion interactions with higher interaction leading to higher viscosities. Increasing alkyl chains have positive effect on the viscosity due to the increasing van der Waals forces. Delocalization of the charge, for example by substituting a fluorine group on the anion or cation, have the opposite effect on the viscosity because it weakens the hydrogen bonds in the ILs. Also, the size and the molecular weight of the ions dictate the viscosity. Research has shown that the anion structure has a larger effect on the viscosity, but the reason for this is not yet been ascertained [3],[10],[11].

1.5.9. Ionic conductivity

This property is governed by the mobility of the ions, which is dependent on the viscosity and the number of charge carriers. The latter is influenced by the molecular weight, the density and the size of the ions. An increase in the viscosity of the IL has the adverse effect on the conductivity, since this decreases the mobility of the species in the ionic liquid. Ion association will decrease the ionic conductivity because it decreases the number of ions that can diffuse. Ionic liquids with more delocalized charges and fewer ion-ion interactions will have higher conductivities. PILs and protic molten salts are reported to have ionic conductivities that are similar to those of aqueous systems [3],[11]. The typical value for the conductivity of an ionic liquid lies between 10^{-4} and 1.8×10^{-2} S cm^{-1} [24].

1.5.10. Ionicity

Like mentioned in section 1.3.2., it is important to know the ionicity of the ionic liquid. AILs completely exist of ions whereas PILs exhibit dynamic acid-base equilibria. Therefore, the ionicity of PILs is more complex than the ionicity in AILs. The problem with this is that there is no standard method to determine the ionicity. An ionic liquid is considered pure if it has less than 1% neutral species [3],[11].

There are multiple techniques that can be used to provide information about the ionicity. These techniques include NMR, changes in thermal properties as a function of the stoichiometry, infra-red spectrometry and ionic conductivity in the form of the Walden plot [11].

The Walden rule relates the mobility of ions to the fluidity of their surrounding medium. This relation can be expressed with Equation 4 [25]:

$$\Lambda\mu = k \qquad (4)$$

Where Λ is the ionic conductivity, μ the viscosity and k a temperature dependent constant. On the logarithmic plot of the molar conductivity in function of the fluidity ϕ ($\phi = \mu^{-1}$) one can compare the tendency to form ions of non-aqueous solutions, ionic liquids and molten salts. An "ideal" reference line can be constructed using dilute aqueous KCl solutions and this line represents independent ions with no ion-ion interactions. The proximity to this line is an indication of the ion-ion interactions between the anions and cations in the ionic liquid [25]. All these techniques give qualitative measurement of the ionicity [11]. However, it has become clear that the Walden plot is unable to distinguish if the cause of the low ionicity is due to a low degree of proton transfer or if it is the result of ion pairing [12].

The ionicity can be quantitively determined as the ratio of the molar conductivity measured by impedance and the one measured by pulse-field-gradient spin echo (PGSE) NMR ($\Lambda_{imp}/\Lambda_{NMR}$). Λ_{imp} can obtained by dividing the ionic conductivity by the molar concentration of the PIL. Λ_{NMR} can be obtained with the Nernst-Einstein equation (Equation 5) [3]:

$$\Lambda_{NMR} = \frac{F^2}{RT}\,(D_{cation} + D_{anion}) \qquad (5)$$

F and R are the Faraday and the ideal gas constants, T is the absolute temperature in Kelvin and D corresponds to the diffusion coefficients of the cation (D_{cation}) and the anion (D_{anion}). The latter can be experimentally determined by PGSE-NMR measurements [3].

1.5.11. Polarity

The polarity is one of the more important properties of ionic liquid to characterize the solvent effect in chemical reactions. It is probably the most widely discussed property of ionic liquids since there is no parameter or direct measurement that can characterize the polarity. There is the possibility of using solvachromic dyes to determine empirical polarity parameters, but they are most likely not truly independent from the probe molecule that is used. The difficulty for ionic liquids is finding a suitable soluble probe which measures the polarity parameters as independent as possible from the influences of the solvent [7].

For protic ionic liquids, the polarity has been determined by using solvent probes with chromatography and was then compared with traditional organic solvents. In general, PILs have shown to be highly polar solvents. Primary and secondary ammonium based PILs are the most polar ionic liquids with polarities similar to the polarity of water. Ionic liquids based on tertiary ammonium cations had slightly lower polarities [11].

1.6. Properties of DESs

1.6.1. Toxicity and biodegradability

The toxicity of DES is low to non-existent and their biodegradability is extraordinarily high. Beside this they also have the highest possible atom efficiency. These properties combined with the fact that these solvents originated from mostly renewable resources, gives them a minimal ecological footprint [17], [26].

1.6.2. Viscosity

The viscosity of DESs is similar to those of the ionic liquids. The viscosity can be lowered by adding a third component to produce a ternary system. Another way to decrease the viscosity is by increasing the free volume of the species, which can be achieved by using smaller ions, like small quaternary ammonium cations or fluorinated HBDs. DES show their lowest viscosity at the eutectic composition [5], [18].

1.6.3. Density

The density is just like the viscosity similar to those of ionic liquids, which is together with the viscosity an obstacle for industrial application. The density can be lowered in the same way as the viscosity can be lowered, by adding a third component to generate a ternary mixture [18].

1.6.4. Solvation properties

DESs exhibit some unusual solvation properties that are heavily influenced by hydrogen bonding. This directly results in a high affinity for components that are able to donate electrons or protons. As a consequence, protic solvents, such as water and alcohols, tend to be miscible with DESs, whereas aprotic solvents are immiscible. There are only some deep eutectic solvents that are immiscible with water, but this group is limited [18]. This immiscibility of this limited group makes then good solvents for the extraction of aqueous mixtures of chemicals that are difficult to separate from water, like alcohols, by other means, such as distillation. Besides this, the polarity of the DESs can also exhibit a range of polarities, from a dielectric constant of 4 (similar to $CHCl_3$) to a dielectric constant higher than 80 (water), depending on the reagents that are used, which can then be tuned to make them better solvents for specific compounds. There is also possibility to form microemulsion, with or without surfactant, which ensures at least a partial solubility of the aprotic and non-polar compounds [5].

1.7. Applications of ionic liquids and DES

1.7.1. Organic synthesis

A wide range of ILs have been used as solvent or catalyst in different organic reactions. Most of the reactions where ILs are used as catalyst are acid catalyzed reactions. PILs have a proton readily available on the cation, but there also Brønsted acidic ILs, where there is a proton available on the anion or on a functionalized group on the cation. The behavior of these ILs is similar to the behavior of PILs. Brønsted acidic AILs are usually functionalized for this purpose by attaching a sulfonic acid or carboxylic acid group to the cation. The use of ionic liquids typically involves trialing a large number of ILs to achieve the desired activity [11].

There are potential benefits in using ILs that cannot be ignored. The main driving force is the replacement of traditional organic solvents and highly acidic catalysts with these ILs. Brønsted acidic ILs have been found to give good yields and selectivity in a number of different organic reactions. These ILs can also be recycled and reused up to three to five times without or with little loss of activity. The recycling of ILs is discussed in section 1.10 The organic reactions with the use of traditional catalysts involve large amounts of acidic waste and waste solvents [11]. Some organic reactions in which ionic liquids can be utilized are given in Figure 19, Figure 20 and Figure 21.

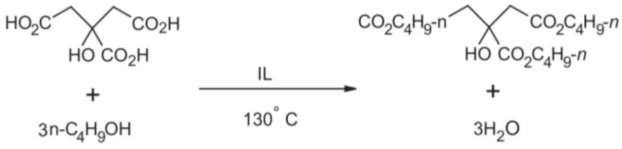

Figure 19: Esterification reaction with an acidic IL as catalyst [27]

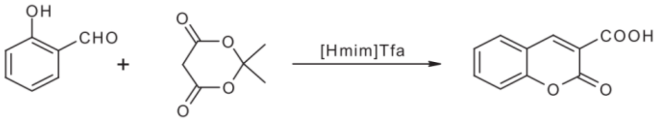

Figure 20: Knoevenagel condesation using the IL 1-methylimidazolium trifluoroacetate as catalyst [24]

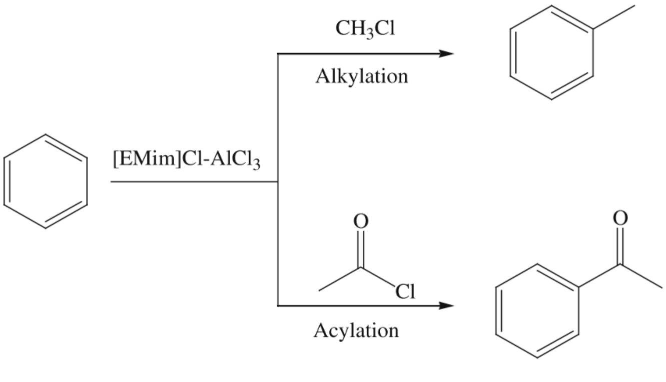

Figure 21: Friedel-Crafts alkylation and acylation catalyzed by the IL 1-ethyl-3-methylimidazolium chloride-aluminiumtrichloride [25]

One of the key properties of the Brønsted acidic ILs and the PILs is their Brønsted acidity. Different techniques have been utilized to determine the acidity. For ILs with the same cation, the acidity is determined by the basicity of the anion. This property can also be determined by using H-NMR by correlating the NH shift for the available proton with the acidity, where a larger shift indicates a higher Brønsted acidity. Another method is using the Hammett acidity scale where the absorbance of protonated and unprotonated indicator is measure in a solution of the ILs, the indicator and an aprotic polar solvent with an UV-VIS spectrometer [11],[12].

Not only ionic liquids, but also deep eutectic solvents have been used as solvent/catalyst in organic reactions. Some acids and bases that are used as catalysts in organic reactions are utilized in the synthesis of DES. Thus, DES cannot only be used as solvent for organic reactions, but also as catalyst in some reactions. One of the reactions that can be catalyzed by DES is the Fischer esterification of long-chain carboxylic acids with long-chain alcohols (> C_{10}). Normal acid catalysts, such as sulphuric acid or HCl, have difficulties with the esterification, however the DES based on ChCl and zinc chloride in a molar ratio of 1:2 can catalyze the esterification of carboxylic acid and alcohols with a chain length between C_8 and C_{22} with a conversion of more than 90 % (Figure 22) [5].

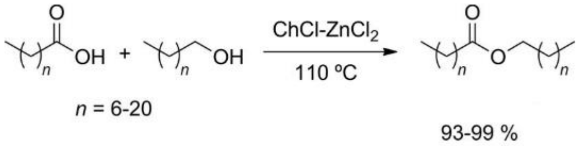

Figure 22: Esterification of long-chain carboxylic acids and alcohols with ChCl-ZnCl$_2$ as catalyst [5]

1.7.2. Chromatography

PILs are of interest as stationary phase in both liquid and gas chromatography and for their use in the mobile phase in liquid chromatography. The properties that make PILs potentially useful as modifiers for mobile phases are that they are polar and can be miscible in water and the ones that make them useful as stationary phase are that they can be moisture/air stable and they have a high selectivity towards solutes that are polar and/or hydrogen donors or acceptors. PILs cannot be used directly as mobile phase due to their high viscosities, so they need to be mixed with water or an organic solvent. The detection of chemicals is usually achieved by using UV absorption spectroscopy. This puts a limit on the anions and cations that can be used to produce the modifier for the mobile phase, since they are required to have no or a minimal absorbance in the visual spectrum (400 – 750 nm). Ionic liquids with imidazolium cations and inorganic anions, such as nitrate, should be avoided because these ions absorb UV-radiation at a specific wavelength [11].

Experiments showed that highly polar PILs have a solvent behavior that is similar to that of solvents with a high cohesive energy. These experiments also showed that these highly polar PILs have dipole-dipole interactions with polycyclic hydrocarbons that are like those with organic solvents. The solvent properties can be adjusted by making changes to the structure of the anion and/or cation. For example, increasing the alkyl chain length will make the PILs behave more like an organic solvent, while decreasing the chain length makes them more water-like.

Alkylammonium nitrate PILs proved useful as mobile phase when combined with solvents with a low viscosity and they showed no significant absorption above 260 nm. ILs mixed with organic solvents resulted in mobile phases with better selectivity and that were able to elute the components more quickly than ILs mixed with water. Mixtures of alkylammonium methanoate PILs with water proved to be good replacements for organic solvents. The mixtures of the IL ethyl ammonium acetate (EAA) and water showed also great potential with polarities that come close to the polarity of methanol [11].

The PILs ethyl ammonium nitrate (EAN) and propyl ammonium nitrate (PAN) have also been studied as stationary phases for liquid chromatography. They were coated on a stationary support and then used in combination with various mobile phases based on organic solvents. These systems worked well, especially for separating isomers with functional group that allow hydrogen-bonding. The same stationary phases as for the liquid chromatography (EAN and PAN) have been trialed here. They proved to be exceptionally useful to separate solutes that are capable of hydrogen bonding, however, solutes that form very strong hydrogen bonds, such as amines, could not be eluted due to too strong interactions with the PILs [11].

1.7.3. Protein stabilization and solvation in protic ionic liquids

Proteins have the tendency to form aggregates during processing which form complications for their reconstruction to their original form. It is a well-known fact that each protein has a pH range in which the original form is more preferred. A deviation from this pH range will affect the stability of the protein and causing them to fold, which can lead to undesirable behavior like aggregation and fibrillization. This means that the proton activity in the PILs will have a strong effect on the stability of the proteins. This opens the possibility of preserving normally fragile proteins indefinitely at ambient temperatures by determining the optimal proton activity and using the PIL that possesses this proton activity. This can have its use in the preservation of enzymes for enzyme-catalyzed reactions [28].

The potential applications for the use of ionic liquids, more in particular EAN, in the solvation of proteins have been investigated. These applications include dissolving hydrophobic ligands to incorporate them in protein crystals, improving the solubility of some proteins, improving the mono-dispersity of proteins for the use as precipitating agent and as additive. Experiments with the PIL EAN showed that it can prevent the aggregation of these proteins. The explanation for this is that EAN has a weaker attraction to the hydrophobic part of the proteins, for low concentrations this resulted in an easier displacement of the EAN during the refolding of the protein. This means that there has to be compromise in the concentration of EAN since too high concentrations result in more difficulties in displacing the ion to refold and too low concentrations resulted in aggregation [11].

1.7.4. Antimicrobial

Protic ionic liquids with the 1-alkyl- and 1-alkoxylmethylimidazole cations combined with lactate or salicylate anions were successfully applied in antimicrobial applications due to their toxicity. This will result in a PIL with a high packing disorder, which results in a low melting point. The minimum concentration to inhibit growth of bacteria decreased with the increasing chain length which is in accordance what was discussed earlier under section 1.5.1. Both PILs and AILs showed similar antimicrobial properties, however, the PILs were more environmentally friendly in comparison with the AILs [11].

1.7.5. Liquid electrolytes and membrane electrolytes in polymer membrane fuel cells

A large number of PILs have been developed and characterized to have good ionic conductivities for use as electrolytes in fuel cells. One of the hot research topics has been the improvement of polymer electrolyte membrane fuel cells (PEMFC) [11]. Fuel cells are electrochemical devices that convert chemical energy into electrical energy. These PEMFC were developed to reduce the dependence of electricity production on fossil fuels and the production of pollutants, such as CO_2, NO_x and SO_2. These PEMFCs generate more energy per unit of fuel and have a low emission generation, which allow them to generate clean power [24].

These fuel cells consist of bipolar plates, diffusion layers, electrodes and an electrolyte. The core of the PEMFC is composed of the proton exchange membrane between two electrodes (Figure 23). This core is also called the membrane electrode assembly. The most important properties of this membrane are [24].

- High proton conductivity in dry and wet states.
- Outstanding mechanical strength and dimensional stability.
- High ionic liquid retention.
- Chemical, electrochemical and thermal stability under operating conditions.
- Low crossover of oxygen and fuel.
- Easy conformation to form a membrane electrode assembly.
- Competitive cost.

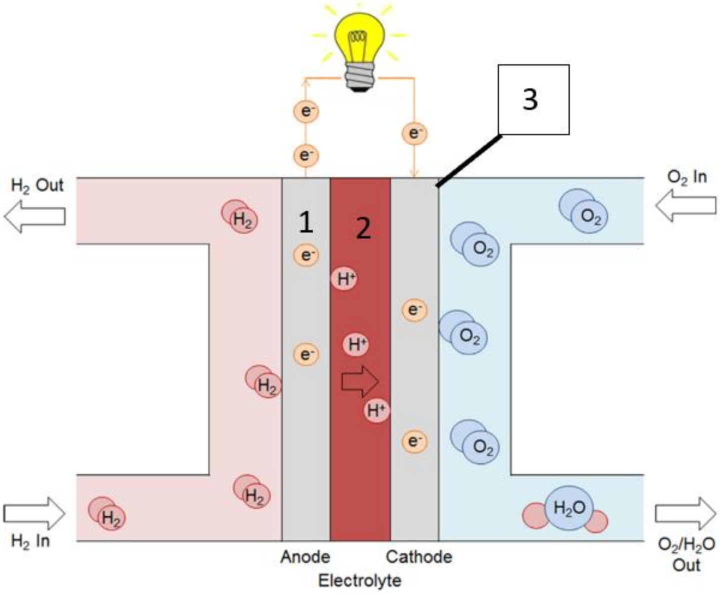

Figure 23: Schematic representation of a PEMFC with (1) the electrode, (2) the electrolyte and (3) the diffusion layer [22]

Currently, nafion polymer membranes (Figure 24) and aqueous electrolytes are the most used membranes and electrolytes in PEMFC. The main disadvantage of these membranes and electrolytes is that they cannot be used at a temperature above 100 °C, which results in complex heat and water management systems and a lower efficiency in the redox reactions [8]. High temperatures are desirable, since this improves the tolerance of the Pt electrodes towards contaminants, which offers the option of using hydrogen with a lower purity. A higher temperature also increases the electrode reaction rates [24].

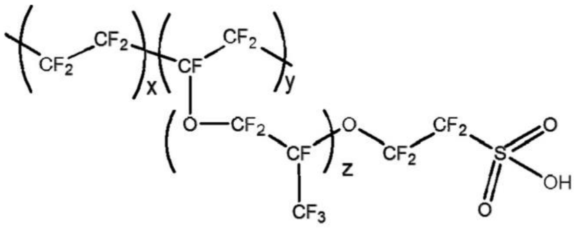

Figure 24: Chemical structure of Nafion [24]

PILs can also be directly used as a liquid electrolyte. The proton migration in most PILs occurs through a vehicular mechanism in which the electrolyte comes together with the membrane to form a proton conducting channel and where the electrolyte acts as “vehicle” for the protons. This implicates that the PILs with the higher fluidities are also the ones with the highest conductivities. The benefit of using these materials is that they can be operated at temperatures above 100 °C under anhydrous conditions. There has been a lot of attention of ammonium based PILs, while phosphonium have not received as much attention. Phosphonium based PILs have shown to be superior in terms of viscosity, conductivity and chemical and thermal stability. This is directly related to their weaker hydrogen bonds and coulombic interactions [24].

However, solidified electrolytes are preferred when using ionic liquids. This is because most electronic devices require electrolyte materials in the form of a film. This can be achieved by producing polymer-ionic liquid membrane electrolytes that have the function of both electrolyte and membrane. Using the ionic liquids in this form results in an improvement of the transport properties of the polymer. This is the result of the modification of the ion dissociation degree , concentration of ionic moieties and the glass transition temperature [24].

The production of these membranes can be achieved by doping the polymer with ionic liquids, by crosslinking/polymerization of monomers in the presence of ionic liquids or by polymerizing ionic liquids to form polymerized ionic liquids. The first process can be done in two ways: Solvent blending or impregnation synthesis.

In the solvent blending synthesis (Figure 25a), the polymer is synthesized and blended with the IL in an appropriate solvent to form a homogeneous mixing solution, which is cast in the required shape and dried to evaporate the solvent. This method is utilized in combination with homopolymers, copolymers, hydrocarbon polymers and block copolymers. The way of synthesis allows an easy control of the conductivity by adjusting the ionic liquid content.

The impregnation synthesis (Figure 25b) requires a pre-prepared polymer membrane, which is submerged in the IL to absorb it. It is a simple way of producing polymer-ionic liquid membranes, but the pre-prepared polymer determines the morphology of the final product. This makes this method limited and makes it not possible to tune the interaction between IL and polymer. Moreover, there is also a limitation in the amount of the ionic liquid can be incorporated in the membrane, since higher amounts are desired for a better proton conductivity.

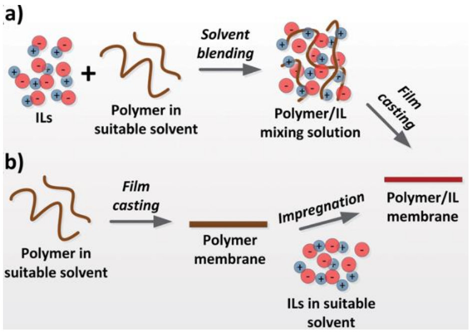

Figure 25: Doping of the polymer with ILs via (a) solvent blending synthesis and (b) impregnation synthesis [8]

For the crosslinking/polymerizing method there are also two pathways: In situ radical polymerization of vinyl monomers in ILs (Figure 26a) and polyaddition of (macro-) monomers in ILs (Figure 26b). In both cases the ionic liquids and the monomers were mixed before polymerization or crosslinking [8].

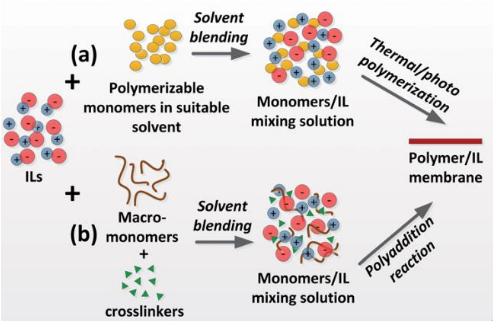

Figure 26: Crosslinking/polymerizing synthesis method via (a) In situ radical polymerization and (b) polyaddition [8]

However, implementing ionic liquids in PEMFCs by the blending or crosslinking/polymerization method requires a compromise between the desired properties of the ionic liquid and the mechanical stability of the membrane. The preparation of IL-based polymer membrane electrolytes is highly depended on the compatibility of the ionic liquid with the polymer. This compatibility is determined by the morphology of the polymer and the anion and cation of the ionic liquid. The disadvantage of this method is that it requires the purification of both the monomers and IL [24].

The final way to produce IL-based polymeric membrane electrolytes is by the polymerization of ionic liquids with a vinyl group. Polymerized ionic liquids can have a wide variety of structures. Depending on the final application they can form different systems, such as polycationic ILs, polyanionic ILs, polymer complexes, copolymers and polyzwitterions (Figure 27).

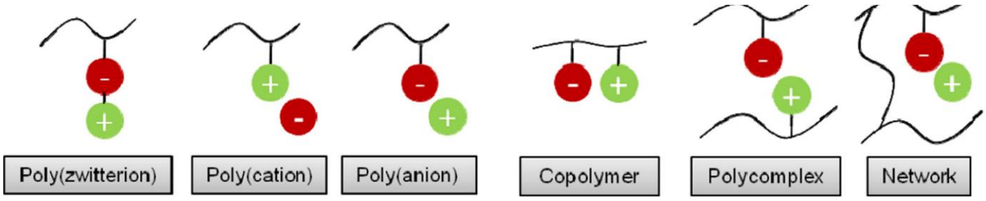

Figure 27: Possible types of polymerized ionic liquids [24]

There are two ways to perform the polymerization of ionic liquids: direct polymerization of the IL monomers and modification of a polymer via anion exchange (Figure 28). The direct polymerization is most frequently performed via free radical polymerization due to its high tolerance towards other functional groups, moisture and impurities. The monomers that are most often used usually contain (meth)acryloyl, styrenic and N-vinylimidazolium groups. Recent advancements have shown that it is also possible to prepare these membranes via controlled radical polymerization. This method allows control over design and macromolecular architecture of the IL species. It even gave the opportunity to produce block copolymers [24].

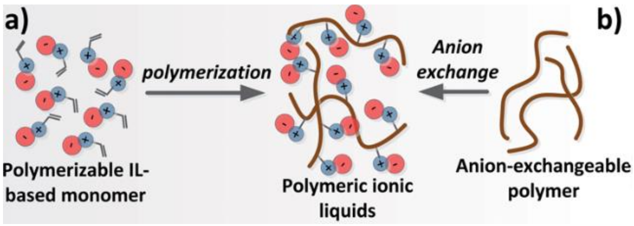

Figure 28: Synthesis of polymerized ionic liquids via (a) polymerization of ILs and (b) anion exchange [8]

The main pathways to achieve the modification are grafting of N-alkyl imidazole onto the halo-alkyl function present on each repeating unit and the reaction of the imidazole groups on the polymer with a halo-alkane. The disadvantage of this method is the decrease in the number of mobile ions and their mobility, since the anion or the cation is attached to the polymer chain. This problem can be simply solved by increasing the amount of mobile ions by adding more ionic liquid, but this compromises the mechanical stability [24]. This method has the advantage that it is quite simple when compared to the previous one, since it only requires the purification of one monomer and the polymerization step/ modification step [8].

1.7.6. Explosive formulations

Alkylammonium nitrate ILs are known for their highly explosive and exothermic decomposition upon heating. The main decomposition products of this type of PILs are H_2O, NO, NO_2, N_2O, CO and CO_2. Experiments showed that heating at low pressure caused this decomposition to happen endothermically with the first step of the decomposition being the proton transfer to make amines and nitric acid. These experiments also showed that a more complete decomposition of the PILs is obtained if there is more alkyl substitutions on the ammonium cation of the PIL.

This explosive nature gave birth to a range of explosives and propellants based on these alkylammonium nitrate PILs. PIL-based explosives were created by making a mixture of the PIL, an inorganic nitrate, water, a non-explosive sensitizer and a thickening agent. The important difference between traditional explosives and explosives based on PILs is that the sensitizer (the chemical that promotes the rate of propagation of an explosive material) itself is not explosive in PIL-based explosives, whereas the traditional explosives required something like trinitrotoluene.

Next to explosives based on PILs, there is also a growing interest in monopropellants based on PILs. Monopropellants are propellants that consists of chemicals that release energy due to exothermal decomposition. The advantages of these propellants are that they are non-flammable, easy to handle, less corrosive than traditional monopropellants, have no organic vapor emission and do not contain hydrazine or hydroxylammonium nitrate. The cost of the PILs based monopropellants are about one third of the traditional ones [11].

1.7.7. Lubricants

A couple of imidazolium based AILs and alkylammonium PILs have been tested for their potential use as lubricants in steel on aluminum applications. The PILs appeared to be superior to the AILs. The PILs showed a lower friction coefficient than the traditional hydrocarbon-based lubricants, but they also showed a higher wear of the aluminum. These ionic liquids reacted fast with the metallic surfaces and formed a boundary film. This fast reaction also implicates that more material is being used, and hence, there was a higher wear observed. PILs have also been researched as additives in traditional lubricants. These lubricants showed both decreased friction and wear in the same application of steal on aluminum, which leads to the conclusions that it is more beneficial to use the PILs as additives instead of using them as a lubricant. However, there was no mention of the effect on the price of the lubricants [11].

1.7.8. Capture of carbon dioxide

Aqueous alkanolamines are widely used for the removal of CO_2 from industrial flue gas. One of the most used alkanolamines is 2-hydroxyethylamine for its low cost, reasonable thermal stability, low thermal degradation rate, high reactivity towards CO_2 and low molecular weight. However, these alkanolamines are far from ideal due to their corrosive nature, recovery and losses resulting from their relatively high vapor pressure. The high solubility of CO_2 in room temperature ionic liquids and DES offers the possibility to exploit them in different media for CO_2 capturing. However, their physical properties, such as their viscosity and thermal stability, will ultimately decide their suitability for industrial applications.

1.7.9. Pretreatment of lignocellulosic material

The decreasing fossil fuel resources, the demographic increase and the environmental concerns have caused many countries to make the transition to alternative energies. In the past, the main focus was put on the transformation of oils in biofuels. However, the last couple of years the main discussions in this field shifted to the conversion of biomass into transportation fuels and valuable chemicals, due to the limited resources of triglycerides and ethical reasons. Lignocellulosic materials rapidly appeared as one of the most interesting carbon neutral, renewable, cheap and abundant resources [7]. The feedstocks that can provide this lignocellulosic biomass are: wood resources (like wood waste from saw and paper mills, but also forest arisings such as branches, bark and stumps), Agro-industrial and agriculture residues (sugarcane bagasse, rice or wheat straw, rice husk, spent coffee grounds, etc.) and dedicated energy crops (energy tobacco, switchgrass, miscanthus, etc.) [29].

Currently, most of these feedstocks are wasted or incinerated for energy. Bio-refineries usually use bio-chemical technologies, such as fermentation or enzymatic procedures, to convert lignocellulosic biomass in these feedstocks into building blocks. Chemical processes are then used to turn these building blocks into molecular derivatives and intermediates. The most often used chemical processes are reduction, hydrogenation and selective dehydration. The potential of catalysis is important in this field to progress towards more environmental processes or to achieve a more selective and more efficient synthesis under ambient conditions. The development of catalysts with an improved stability and a better tolerance towards biomass impurities is necessary. ILs display interesting properties like their reasonable chemical inertness, their decent thermal stability, their low volatility and, the important property for this application, their unique solvation abilities [7].

Lignocellulosic biomass is built up of cellulose (33–45%), hemicellulose (20-30%) and lignin (15-30%) (Figure 29) and can be a valuable resource. The main obstacle is the separation, recovery and processing of all its fractions in a cost-effective way. The pre-treatment of lignocellulose can be the key to a successful conversion of its fractions into sugars or via enzymatic or catalytic hydrolysis into biofuels. A number of treatments, such as acid-base methods, steam pre-treatments, solvent extraction methods and ammonia-based methods, have been utilized, but these generally showed high costs and an incomplete fractionation of the lignocellulose. The main goal of all these pre-treatments is to make the all fractions available for enzymatic conversion, however, there exist limiting factors that hinder the accessibility to the enzymes. These limiting factors can be categorized in two groups: biomass structural features and the enzyme mechanism [7].

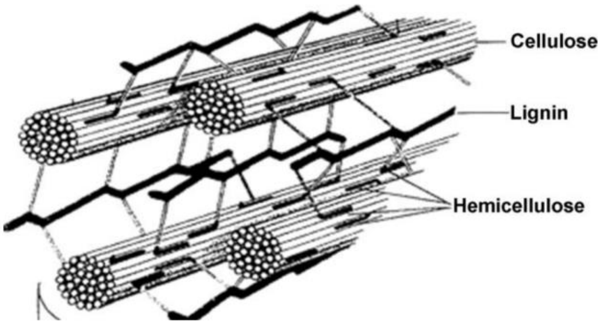

Figure 29: Structure of a lignocellulose network [7]

The resistance of the lignocellulosic biomass towards enzymatic hydrolysis can be attributed to the accessibility of the surface, the protective lignin, the degree of polymerization and the biomass particle size. The presence of lignin and the crystallinity of the cellulose are the main hindering factors. The presence of hemicellulose on the surface of the cellulose is another factor that decreases the accessibility. The pre-treatment of lignocellulose would enable an improved enzyme usage in the hydrolysis with possible regeneration, an improved lignocellulosic biomass fractionation and amorphous cellulose generation, which is can be converted much faster into sugars and biofuels. The improved enzyme usage would lead to higher sugar yields with a lower formation of inhibitors and a lower sugar degradation. The fractionation of lignocellulosic biomass allows a better economy and the option to use a diversity of biomass feedstock. Choosing the appropriate pre-treatment is often a compromise between minimizing the degradation of cellulose and maximizing the ease of enzymatic hydrolysis [7].

Dissolution of lignocellulose has been investigated, but not as abundantly as the cellulose dissolution. Two parameters are essential for solubilization. The first is the particle size of the biomass, which involves the compact and complex structure that inhibits the diffusion of the IL into the interior resulting in partial dissolution. The second is water content where a higher water content results in a lower solubility in ionic liquids [7].

The monomer units of lignin (p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol), cellulose (glucose) and hemicellulose (Mannose, xylose, glucose, galactose, arabinose and glucuronic) (Figure 30) are connected with each other via hydrogen bonds [30], [31]. This is what makes the lignocellulose such a strong structure. The ionic liquid disrupts the hydrogen bonds in the complex matrix of the lignocellulose. This is mostly attributed to the anion that from strong hydrogen bonds with the carbohydrates. ILs have potential to pre-treat lignocellulosic biomass, however, there are two challenges that need to be overcome:

the recovery and reuse of ILs and the recovery of lignin and hemicellulose from the ILs after the cellulose has been extracted [7].

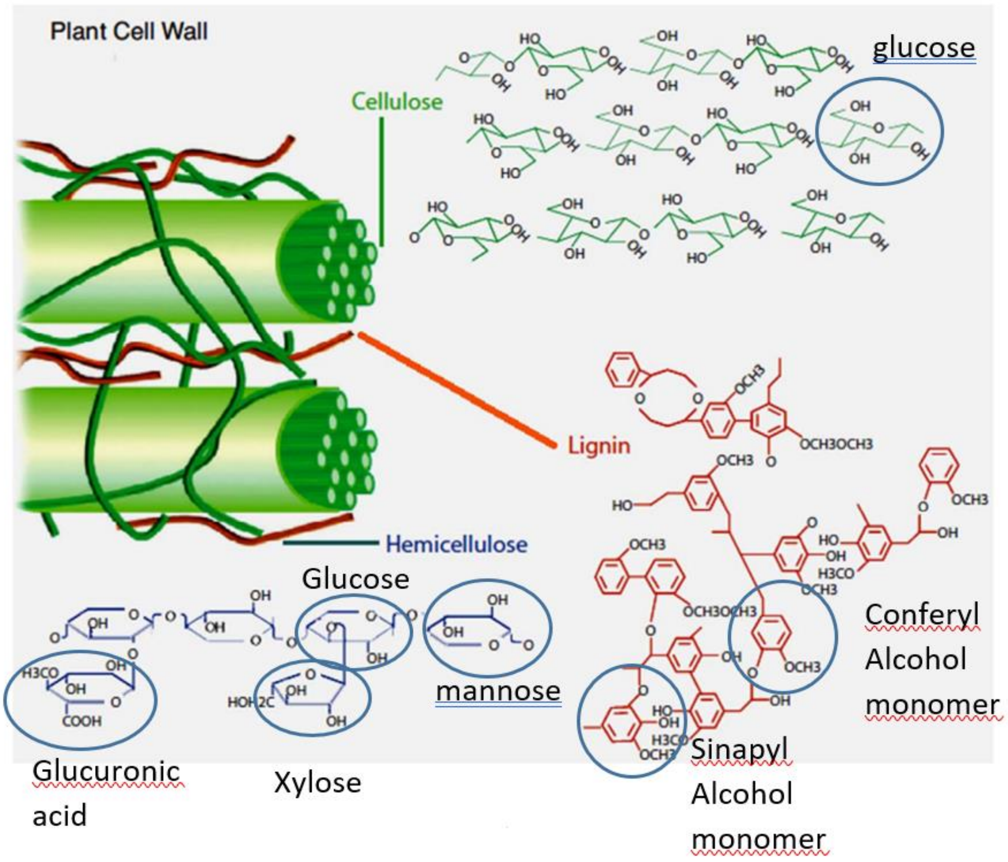

Figure 30: Structures of the fractions and their monomer units (except p-coumaryl alcohol for lignin and galactose and arabinose for hemicellulose) [32]

The acid catalyzed hydrolysis of cellulose (Figure 31) is not a new technology but is not yet cost-effective for large-scale applications. There are several main issues such as harsh conditions, undesirable degradation of cellulose, the need for corrosive resistant equipment and the disposal problem of concentrated acid processes. The use of ILs as acid catalysts can resolve most of these problems. By dissolving the cellulose in the IL, the protons in the IL can more easily access the β-glucosidic (bonds between the glucose molecules) bonds to perform the hydrolysis. It seems that by dissolving the cellulose in the IL, the “physical” lignin barrier can be overcome. This promotes the acid-catalyzed hydrolysis at relatively lower temperatures and lower catalyst amounts.

The model compound cellobiose was used to determine the optimal conditions for the hydrolysis of cellulose with an IL as catalyst. The optimal conditions were an IL based on a strong acid, a water content between 5 and 10w%, carbohydrate content less than 10w% and a temperature between 80 and 150 °C. The hydrolysis was also tested for lignocellulosic material, The results of this research showed that optimized sugar yields are obtained when the lignin extraction and the hydrolysis in these conditions are combined [7].

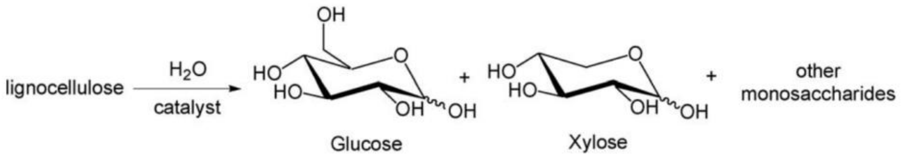

Figure 31: General representation of the catalytic hydrolysis of lignocellulosic biomass [7]

The enzymatic hydrolysis involves a series of complex steps. These steps are: (1) The transfer of the enzymes from the bulk aqueous solution to the surface of the cellulose, (2) The adsorption of the enzymes to form enzyme-substrate complexes, (3) The hydrolysis of cellulose, (4) the transfer of glucose and not fully reacted cellodextrin and cellobiose to the aqueous phase and (5) the further hydrolysis of cellodextrin and cellobiose into glucose [33]. The enzymatic hydrolysis is shown in Figure 32. The first to steps are the critical steps in this reaction. Just like in the catalytic hydrolysis, ILs can dissolve the cellulose and make it more accessible for the enzymes and partially hydrolyze via catalytic hydrolysis. The drawback of the use of ILs is that the typically used ILs have the tendency to denaturize the enzymes. With other words, a fine design is necessary so the ILs can dissolve the carbohydrates and does not considerably denature the enzymes [7].

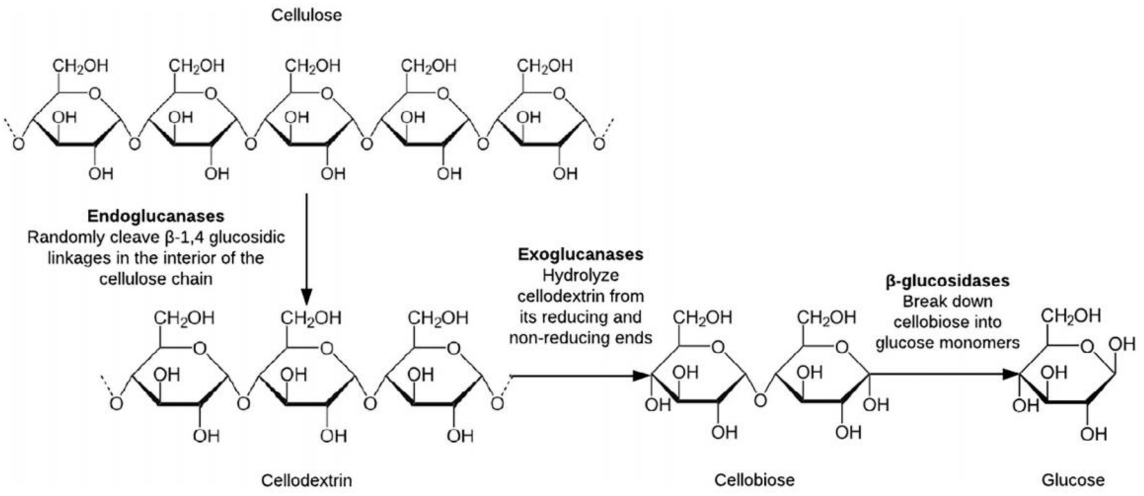

Figure 32: Enzymatic hydrolysis of cellulose in glucose [34]

1.7.10. Desulfurization of fuel

One of the main problems with the use of fossil fuels is the presence of sulfur species in the fuel. These sulfur species can cause faster deterioration of engines and catalysts used for the control of the emissions, when they are left in the fuel. Beside this, sulfur also forms SO_x upon combustion, which contribute to acid rain, ozone depletion and air pollution with major effects on the health of living organisms. For this reason, it is of significant importance to produce fuels with ultra-low sulfur contents. Hereto, the bonds between organic molecules and sulfur need to be cleaved, which requires high temperatures and pressures. This is currently done via hydrodesulfurization which uses hydrogen to turn the sulfur species in H_2S, but this only works for aliphatic and alicyclic sulfur species and is less effective for benzothiophene, dibenzothiophene and their alkyl derivates (Figure 33). There is also the problem with side-reaction such as the formation of cokes and the saturation of olefins [35].

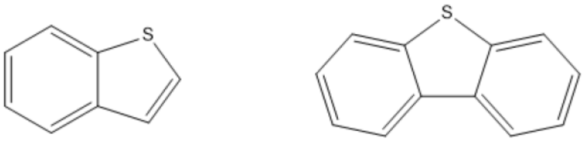

Figure 33: Structures of benzothiophene (left) and dibenzothiophene (right)

Extractive desulfurization is a well-established process that can be performed at ambient temperatures and pressures. The extractant needs to have a boiling point different from the sulfur species, the sulfur species need to be highly soluble and preferably inexpensive. Ils have been investigated as extractant. They showed high extraction ratios and a high selectivity compared to traditional solvents, however, the high cost, the high viscosity, their uncertain toxicity and the low tolerance to moisture make them not suited for this use.

DES, Cholinium Chloride-glycerol (1:2) (Figure 34) to be more specific, were also investigated for this purpose by *Zaid et al (2016)*, since they have a lower cost than ionic liquids and they are non-toxic. This studied DES showed an extraction of 97.06% of the model compound dibenzothiophene-sulfone (Figure 35) from dodecane after 20 minutes and a complete removal after two cycles. The optimum conditions for this extraction were a stirring speed of 300 rpm, 20 minutes of extraction time and a volume ratio of DES to model compound of 1:5 [35].

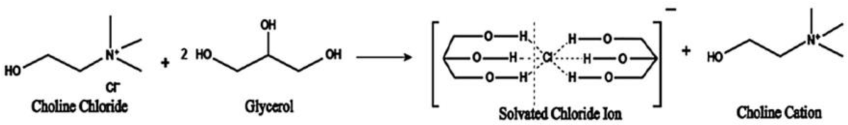

Figure 34: Structure of cholinium chloride-glycerol [35]

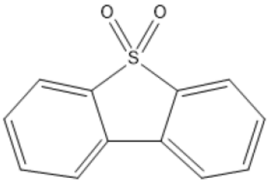

Figure 35: Structure of dibenzothiophene-sulfone

1.7.11. Extraction with DESs

Like mentioned earlier, DESs possess a strong ability to donate or accept electrons or protons. This makes DESs excellent solvents to dissolve a wide variety of substances including salts, proteins, drugs, amino acids, surfactants, sugars, polysaccharides and also various metal oxides. This solvation property makes them ideal for extraction [18]. DESs have already been successfully tested in the extraction of glycerol from biodiesel, the denitrification of diesel, extraction of volatile fatty acids, in the solid-liquid extraction of organic acids, bioactive compounds from various plant materials and many more [18], [17], [15], [4].

1.8. Chemical recycling/valorization of poly (lactic acid)

The majority of plastics are created from fossil fuel resources, while only a small fraction is derived from renewable resources. These fossil fuel resources are not only decreasing, but are also related to global warming. The transition to bio-based plastics is needed, especially when considering the increasing demand for plastics. Another important issue of plastics is the pollution caused by end-of-life mismanagement [36]. This is also the case for bio-based plastics, which are considered biodegradable, since the degradation can still take up to a couple of years. The current use of plastics follows a linear model, where the plastics is produced, used and disposed. The future plastic use needs to be based on a circular model, in which the value of the material is retained after its useful lifetime.

Poly (lactic acid) (PLA) is a bio-based polymer that got a lot of attention the last 20 years. The monomer, lactic acid, is derived from renewable feedstocks through fermentation which is currently more expensive than the production of plastics from fossil fuel resources. The production of PLA via the polymerization of lactide is preferred over the polycondensation of lactic acid since the latter process is limited by the need to remove water, that is formed as by-product, and generally leads to the production of PLA with lower qualities. The production of lactide from lactic acid is a two-step process requiring oligomerization followed by a backbiting process to form the cyclic molecules [37]. This process generates up to 30% of the total cost. Therefore, a lot of research has been devoted to directly produce the dimer. Besides the better quality of PLA, this process also allows the production of PLA with a high molecular weight and does not produce water as by-product. The chirality of both lactic acid and lactide is an important factor that needs to be consided when producing these chemicals and in the subsequent polymerization [38].

There are various options for the end-of-life disposal of PLA (Figure 36). However, the first step is the identification and separation of PLA from other plastics. A common issue is the separation of PLA and polyethylene terephthalate (PET), which are indistinguishable with the naked eye. Near infrared imaging allows the separation of these two plastics [38].

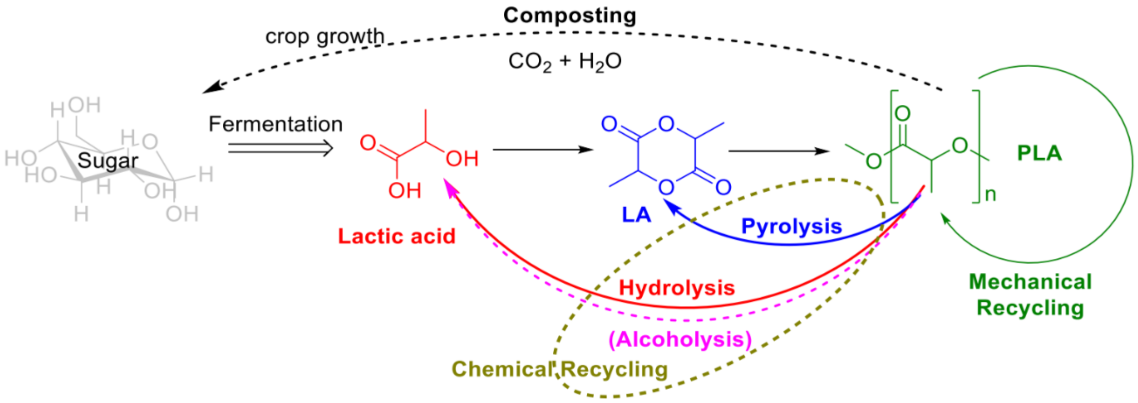

Figure 36: Formation of poly (lactic acid) and the possible end-of-life scenarios (Note: alcoholysis generates an alkyl lactate) [20]

Poly (lactic acid) can be efficiently decomposed in an industrial setting, requiring temperatures around 60 °C and a relatively high humidity. Degradation under these conditions takes about 30 days and produces CO_2 and water. Mechanical recycling is a process in which the plastic is collected, washed and reprocessed into “new” plastics. The reprocessing is typically achieved thermally, which can have a negative effect on the properties of the next generation of the material [39]. This limits the application of the PLA to applications in which lower qualities of plastic can be used. However, after a recycling the PLA a couple of times, the decrease in the properties is so large that it cannot be reused again and has to be thrown away.

Another option is the chemical recycling of PLA. This type of recycling breaks the polymer down into its constituent parts, which can then be reused for polymerization or for other applications. Previous research has shown that this process is energetically more favorable than the production of lactic acid from virgin feedstock. An efficient chemical recycling process can expand the effective lifetime of the material significantly. Another advantage of chemical recycling is its tolerance to contamination by other plastics, since different plastics require different conditions for the hydrolysis. This reduces the need for the expensive separation process. Stereochemistry is an important factor to take into consideration. The more common L-lactic acid isomer is mostly used for the production of PLA, so to avoid further separation or purification steps, which would increase the potential cost, it is important that the stereochemistry is maintained. Chemical recycling of PLA can be done via hydrolysis or via alcoholysis [38].

1.8.1. Hydrolysis of PLA

High temperatures or strongly acid/basic environments are necessary to dissolve the PLA for the hydrolysis. In these media the hydrolysis is achieved by bulk or surface erosion (Figure 37). Which mechanism occurs, is determined by the rate of water diffusion relative to the bond breaking, which is in-turn dependent on the molecular weight, polymer dimensions, pH and temperature. Bulk erosion occurs when the water diffusivity is high and results in a homogenous loss in mass across the whole sample, whereas surface erosion only causes an increased degradation on the surface [38].

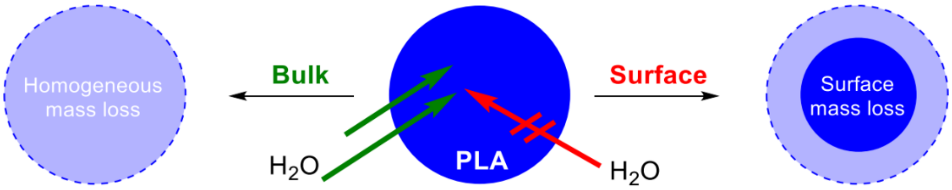

Figure 37: Mechanisms of hydrolysis of PLA [20]

The optimum temperature for the hydrolysis of PLA into L-lactic acid is found to be 250 °C with conversions around 90% within 20 minutes. Above this temperature racemization was observed and at a temperature of 350 °C decomposition of the PLA was observed [40]. The hydrolysis can also be performed by utilizing ionic liquids. The AIL [Bmim][OAc] was found to be the best candidate, allowing a high conversion to lactic acid (up to 94%) within 2 hours at 130 °C, which is higher than the temperature used in a typical hydrolysis (at least 100 °C) . The effect of this ionic liquid on the PLA is shown in Figure 38. The ionic liquid was able to partially dissolve PLA with the ions assisting in the hydrolysis mechanism. To isolate the produced lactic acid, calcium carbonate was added to precipitate calcium lactate. Moreover, the IL could be recycled and reused up to seven times without any loss in performance [38].

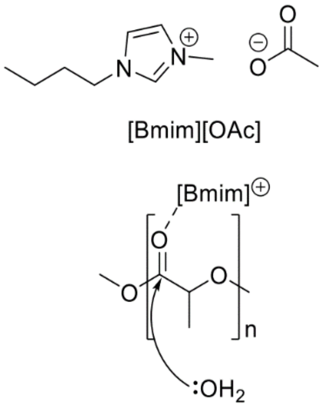

Figure 38: Structure of [Bmim][OAc] and the activation of PLA by this ionic liquid [20]

1.8.2. Alcoholysis of PLA

The alcoholysis of PLA is mostly performed with methanol to form methyl lactate, but it can also be performed with ethanol to form ethyl lactate. Both methyl and ethyl lactate can be used as green solvents with good biodegradability and low toxicity or as a building block to produce other chemicals. These alkyl lactates can for example be transformed into lactide, which closes the loop in the PLA life cycle.

One class of investigated solvents was the 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-based protic ionic liquids. Protonated DBU cations with carboxylate anions (Figure 39a) allowed high degradation yields under mild conditions (100 °C, 5 h). The proposed mechanism describes the [DBU-H] cation activating the polymer carbonyl with the attack of the alcohol assisted by the carboxylate anion through hydrogen bonding/transfer. The DBU-based ionic liquid containing the imidazole anion (Figure 39b) is capable of degrading a range of polyesters and polycarbonates. At relatively low temperature of 70 °C a complete degradation of PLA into methyl lactate was achieved after one hour [38].

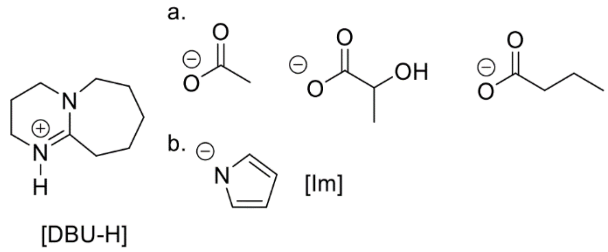

Figure 39: DBU-based protic ionic liquids; (a) carboxylate anions, (b) imidazole anion [20]

1.9. Challenges for industrial application of ionic liquids

After discussing the applications of ionic liquids, it seems that the use of ionic liquids could provide some significant improvements to various existing applications. However, there are certain criteria that need to be met before they can be successfully applied on an industrial scale. Changing a process, which has been proven to work excellent in an industrial setting, by a newer process that uses ionic liquids is not easy even though it could be more profitable in the long run. It requires the willingness to implement these new technologies and products and accept the associated risk. Sometimes new environmental regulations and/or competition may force companies to take this risk. The production cost and the novelty of ionic liquids are the main barriers that prevent companies from implementing applications with these solvents. The price of the IL must be related to the process performance and the overall economy. The main issues with ILs are their short lifetimes (long-term chemical and thermal stability), their loss during the processes as impurities in other streams, their recovery and their recycling. The novelty of ionic liquids raises questions about their toxicity, reliable supply, material compatibility and notification requirements (Registration, Evaluation, Authorization and restriction of Chemicals [REACH]).

In multiphase processes, products are often “simply” separated from the ionic liquid catalytic phase by decantation which allows the recycling of the IL. However, the partial miscibility of ionic liquids in organic products is a source of IL loss and product contamination, which can be a significant issue for the product quality and the process economy. To improve the product-IL separation, different techniques have been investigated. These techniques are discussed in section 1.10.. Some cases allow the use of supported IL processes which utilize ionic liquids immobilized on a solid supporting material. However, these processes fit best when gas-liquid multiphase technology is used, and their application is limited to reactions that involve low volatile reactants and products. The thermal stability was described in the 1.5.4. [7].

The toxicity of ionic liquids has been discussed in section 1.5.1.. When evaluating a process, not only economics should be taken into account but also the sustainability of the process. Sustainability considers the whole process from the raw materials to the purified final products as well as the by-products and the disposal of waste. With other words, the entire life cycle of the ionic liquid needs to be taken into account. The disposal of wasted ionic liquids is often not reported and is a major concern. The incineration of ionic liquids has been suggested as a way of disposing them [7].

1.10. Recovery of ionic liquids

As already mentioned in section 1.9., it is important to improve the recovery of the ionic liquids to make their use in the industry more beneficial. Some of the methods used for the recovery of ionic liquids are described below.

1.10.1. Distillation

Distillation is considered as the simplest method for the removal of compounds with a low boiling point and a high thermal stability. Distillation is used as the final step in a lot of studies that focus on the recovery and recycling of ionic liquids. In these studies, the steps after the reaction and prior to distillation focus on the removal of catalyst and solid products by filtration, washing and decantation. One of these studies showed that the distillation of the ILs is enhanced in terms of operating time and energy efficiency by utilizing microwave heating [6].

The ionic liquids could also be directly distilled. The ability to be distilled is a beneficial property that most of the protic ionic liquids possess. An ionic liquid is under atmospheric conditions distillable if the boiling point is lower than the decomposition temperature. A vacuum distillation is necessary if the latter is lower. ILs can be present as neutral compounds if there is an equilibrium (by deprotonation and protonation or alkylation of cations and anions) between the ionic species and the neutral species. The neutral species can be easily removed by distillation and the ionic liquid is then reformed upon condensing [6]. This mechanism is shown for PILs in Figure 40.

Ionic liquids can be designed to be distillable, but this requires a compromise between the ability to be distillable and the ionicity. A strong proton transfer is crucial to obtain a good ionicity, while a weakly basic anion is necessary to be able to distill the IL. If this is not the case, there will be decomposition of the ionic liquid before the component boils in an atmospheric distillation [11],[20].

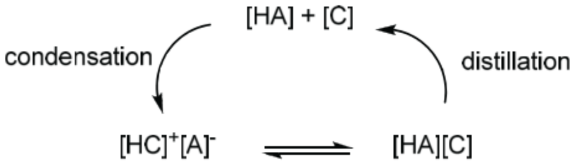

Figure 40: Mechanism for the distillation of PILs [18]

Like mentioned earlier, PILs are easily distillable because they only require heating to moderate temperatures. AILs on the other hand, require higher temperatures and a low-pressure atmosphere to prevent decomposition [11]. AILs are also more likely to be distilled as intact ions, that can be on its own or in an aggregate, instead of being as a neutral species [6]. The mechanism for both types of ionic liquids are shown in Figure 41.

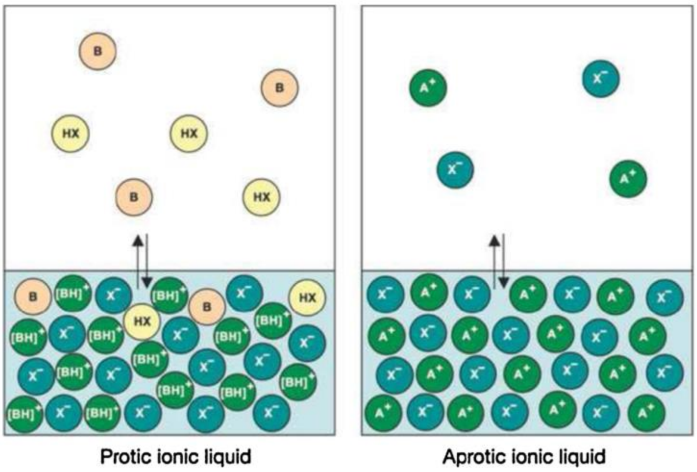

Figure 41: Mechanism for the distillation of PILs and AILs [6]

1.10.2. Extraction

Another frequently used technique is liquid-liquid extraction which is used to remove non-volatile or thermal sensitive products from the ionic liquids. Many molecular solvents, including water, are immiscible with ILs. They form separate phases with ILs and can be used to extracted or separate materials from ILs. The application of ILs in liquid-liquid extraction of metal ions received a lot of attention the last years, because of its potential as "greener solvent" for separation, preconcentration and extraction of metal ions. However, in most cases the ionic liquid was contaminated with highly acid compounds. These contaminations could be extracted by stripping or extraction with a proper organic solvents. This diminishes the "green" aspect of using ILs and can lead to cross-contamination [11].

However, supercritical fluids might be an alternative for the use of these organic solvents. Especially super critical CO_2 ($scCO_2$) is a good alternative because it is nontoxic, non-flammable, environmentally benign and it has a low cost. Perhaps one of its most important properties is that $scCO_2$ is soluble in ionic liquids, but ionic liquids are not soluble in $scCO_2$. Most organic compounds are soluble in $scCO_2$, so the extraction leads to a two-phase system with a $scCO_2$-phase containing the solutes and an IL-phase without any cross-contamination. However, the recovery rate is depended on the dipole moment of the solutes and the amount of CO_2 used. Both of these factors are linked with each other, the lower the dipole moment of the solutes, the better they dissolve in the apolar $scCO_2$, the smaller the amount of $scCO_2$ is necessary for high recovery rates [11].

1.10.3. Adsorption

Ionic liquids can be removed from aqueous solutions, such as reaction mixtures of IL-catalyzed hydrolysis, by adsorption. The adsorption of imidazole based ILs with activated carbon (AC) was investigated. The adsorption capacities were dependent on the size and hydrophobicity of the anion and the cation as well as on the surface chemistry of the AC. The adsorption of hydrophobic ionic liquids was environmentally affordable. The adsorption of hydrophilic ionic liquids could be enhanced by modifying the amount and nature of oxygen groups on the surface of the AC. This method is a robust and relatively easy way to recover ILs from aqueous solutions, however, the requirement an additional desorption solvent is drawback of this method [11].

1.10.4. Induced phase separation

Salting-out is one way to force separation of an aqueous solution of ILs into an aqueous biphasic system. The salt will interact with the water resulting in unavailability of water for interactions with the IL, which causes the system to split into two phases. This has been performed with both potassium-based salts, like K_3PO_4, and sodium-based salts. K_3PO_4 and Na_2CO_3 salts gave the best results. Salting-out is a simple, effective and economical process, since it only requires the addition of cheap salts. However, the high concentration in the salt-containing phase is a mayor environmental drawback [11].

1.10.5. Membrane based separation

Membrane technology is a well-studied field that uses less solvents, which makes it more desirable for industrial application. Non-volatile compounds are usually hard to separate from ionic liquids, since ionic liquids also have a low vapor pressure. Membrane processes make this separation possible which gives them an edge over other separation techniques like distillation. There are two possibilities for separating non-volatiles and ILs: non-volatiles are retained by the membrane whereas the ionic liquid permeates or vice versa. This choice depends on the membrane properties, the size, charge and solubility of the product and the ionic liquid.

Different membrane separation techniques, such as pressure driven membrane separation and electrodialysis, have been investigated, however, all these methods had their own compositions for which they gave an optimal recovery yield. The best option to obtain high recovery yields, is by combining multiple of these membrane processes, but a universal order of processes has not yet been determined [11].

1.10.6. Precipitation by the use of SPS

Like mentioned in section 1.3.4., these are specially designed solvents that can reversibly switch their polarity when a trigger is applied. In this context, the modification of the polarity induces solubility changes of products and/or catalysts, making their purification and separation feasible. One of its applications is the post-treatment in the styrene polymerization. The SPS system used in this application is based on DBU and 1-propanol which uses CO_2 and N_2 as immiscibility and miscibility triggers (Figure 42). Filtration allows the SPS with the catalyst to be reused again (Figure 43) [7].

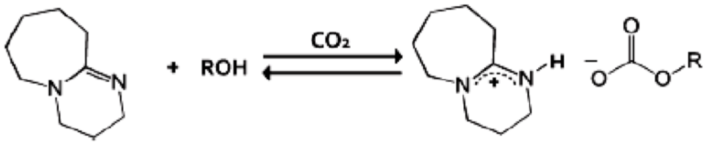

Figure 42: SPS system of DBU and an alcohol [41]

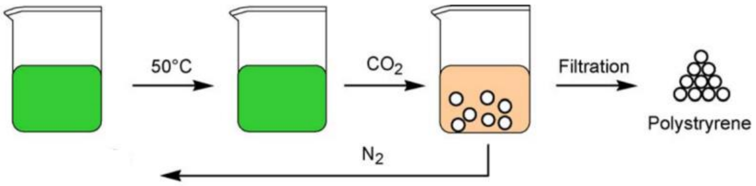

Figure 43: Styrene polymerization in a switchable polarity solvent [7]

Recently a new class of thermally reversible neutral to ionic liquids solvents were described (Figure 44). It is based on siloxylated amines which introduce a weak Lewis acid functionality. These ionic liquids can be converted back to their neutral precursors at moderate temperatures. These solvents can be applied in the recovery of alkanes from heavy crude oil. This process is becoming more and more difficult due to the contaminants, like inorganic salts, in the crude oil, but these impurities can be removed by using one of these SPS. The single-phased homogenous solution of the crude oil and the siloxylated amine-based ionic liquid can be transformed by bubbling CO_2 through the solution. The viscosity increases due to the formation of the ionic liquid and the impurities dissolve in the ionic liquid. The "purified" crude oil can then be separated from the ionic liquid by centrifugation with the "purified" oil being the top layer and the ionic liquid with the impurities being the bottom layer. The original neutral solvent can be recovered by heating the IL to the right temperature and can then be recycled after filtration of the precipitated impurities [7].

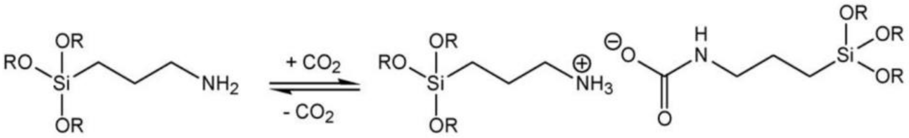

Figure 44: Example of a thermally reversible switchable polarity solvent [7]

1.11. Objectives of this work

The main goal of this work is to synthesize a series of alkanolamine-based protic ionic liquids and a deep eutectic solvent based on L-menthol and decanoic acid for the pretreatment of biomass, as catalyst for the hydrolysis of PLA and as extractant in liquid-liquid extraction of aqueous alcohol mixtures. For this purpose, the most appropriate synthesis method was searched by comparing various methods reported in the literature. Afterwards adjustments were made in the most appropriate method. This method is confirmed by the characterization of the solvents and their properties. Finally, the protic ionic liquids were tested as catalyst in the hydrolysis of PLA to see if they are suitable for this application.

2. Methods and Materials

2.1. Summary of all the methods

A summary of the methods that were used and that would have been used is given in Table 6. The summary is also displayed in a schematic manner in the order the procedures were supposed to be executed in Figure 45.

Table 6: Summary of all the methods

Substance	**Synthesis**	**Purification**	**Characterization**	**Measurements**	**Hydrolysis**
2-hydroethyl ammonium acetate	Yes	Yes	FT-IR; H-NMR	n_D; water content; ρ; μ	N.A.
Bis-(2-hydroethyl) ammonium acetate	*	*	*	*	N.A.
Tris-(2-hydroethyl) ammonium acetate	*	*	*	*	N.A.
DES	Yes	*	*	*	N.A.
PLA	N.A.	N.A.	N.A.	N.A.	With 2-HEAA

N.A.: not applicable; *: Could not be performed due to the Corona outbreak

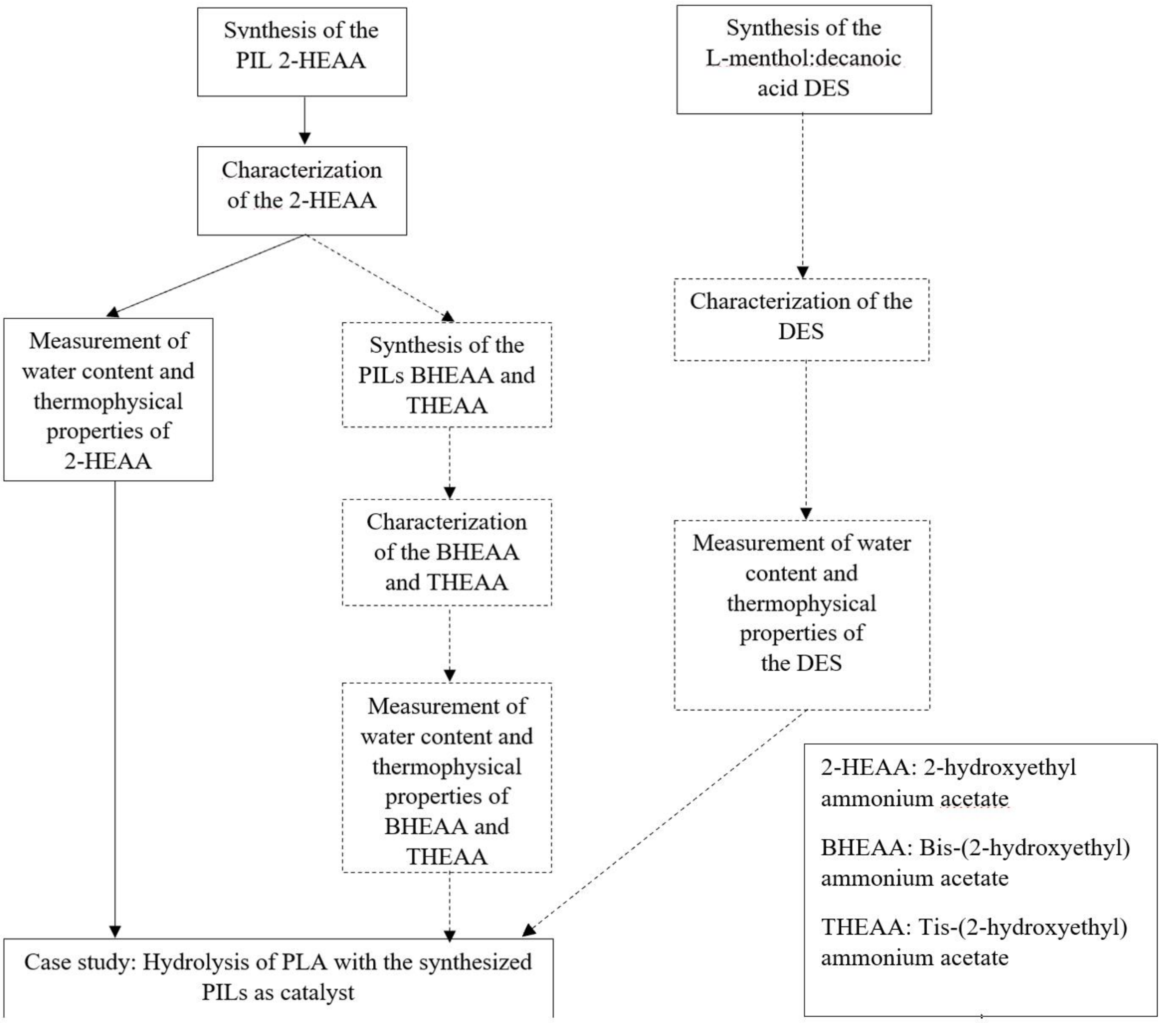

Figure 45: Summary of all the methods that were performed (full lines) and were not performed due to the Corona outbreak (dashed lines).

2.2. Context

The experiments were performed in the laboratories of the Polymer Tecnology and Sustainability Research group of the Department of Chemical Engineering at the *Escuela Técnica Superior de Ingeniería (ETSE)* of the University of Valencia between February and the first two weeks of March. Normally, more time was foreseen to perform the experiments, but this was suspended due to the Corona outbreak.

2.3. Literature study for the synthesis of 2-hydroxylethyl ammonium acetate (2-HEAA)

2.3.1. Comparison of the different synthesis methods

The first synthesis method is the one described by *Kurnia et al.(2009)* [42]. The neutralization reaction of 2-hydroxyethanolamine and the acetic acid (Figure 46) was performed by combining the components at the same time to a three-necked round bottom flask. This flak is equipped with a reflux condenser, a magnetic stirrer and an inlet and outlet for N_2 gas. The reaction mixture was cooled with N_2 gas at a temperature between 5 °C and

10 °C. The mixture was then continuously stirred for 3 hours. Afterwards, unreacted reagents are removed from the mixture by purification under an N_2 atmosphere at 50 °C for 24 to 36 hours. The method described in a later work of *Kurnia et al. (2009)* was identical to the first method. The reason why certain conditions have been selected was not mentioned in both works.

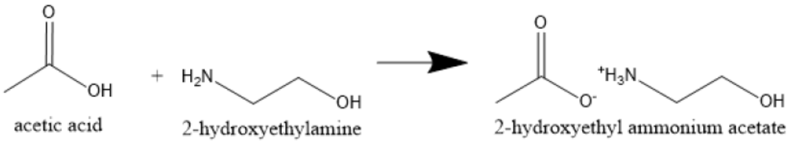

Figure 46: Neutralization of 2-HEA with AA to form 2-HEAA

The next method found in the literature was the one described by *Hosseini et al. (2019)* [43]. They first put the 2-hydroxyethylamine in the two-necked round bottom flask, and then the neutralization reaction was performed by adding an equimolar amount of acetic acid in a dropwise manner. The flask was equipped with a reflux condenser and was mounted in an ice bath. After the addition of the acid, the flask was removed from the ice bath and the mixture was stirred for 20 hours at room temperature. However, it was not mentioned how or if the temperature of the ice bath was controlled. The purification, to remove unreacted reagents, afterwards was done via vacuum drying at a temperature of 60 °C for 24 hours. The synthesis method described by *Ghahramani et al (2020)* [44] was identical to the one described by *Hosseini et al. (2019)* [43]. The reason why these conditions have been selected was not mentioned in the works.

However, there is one group that utilized a synthesis method that is different from all the other and that is the group of *Yuan et al. (2007)* [2]. First, they dissolved the 2-hydroxyethylamine and the acetic acid in ethanol and then performed the neutralization reaction. The setup is similar as described in the other synthesis methods and cooling was done in a water bath that is kept at 25 °C under vigorous stirring. The purification was performed immediately after the reaction. The purification involved evaporating the solvent, dissolving it again for the treatment with active carbon, filtration, another evaporation of the solvent and drying the IL for 48 hours at 50 °C. All these purifications steps make the synthesis more complex and increase the amount of additional impurities, like the ethanol or traces of active carbon, so this method will not be considered.

In literature, 2-HEAA is always synthesized via neutralization of an equimolar amount of 2-hydroxyethylamine with acetic acid and this is always done in a round bottom flask that is cooled during the synthesis. Some studies added the acid completely at the beginning of the reaction and others added the acid in a dropwise manner, but studies stirred the mixture after the addition of the acid. The main differences are the following: The way the flask is cooled during the synthesis, the time the mixture is kept stirring and the method of purifying the IL after the production. A summary of the methods is shown in Table 7.

Table 7: summary of synthesis methods of 2-HEAA found in the literature

Source	**Method of cooling**	**Stirring time**	**Method of purification**	**Purification temperature**	**Purification time**
Kurnia et al. (2009) [42]	Flow of N_2 gas	3 h	Drying under N_2 atmosphere	50 °C	24 – 36 h
Hosseini et al. (2019) [43]	Ice bath	20 h	Vacuum drying	60 °C	24 h

2.3.2. Selection of synthesis method and adjustments

The synthesis of 2-HEAA is performed via the in the literature suggested neutralization reaction of 2-hydroxyethylamine with acetic acid in equimolar amounts. The synthesis will be performed, just like the literature describes, in a three-necked round bottom flask equipped with a stirrer, a dropping funnel and a reflux condenser, which is cooled during the reaction. However, the cooling will be done by placing the flask in a thermostatic bath that is kept at a temperature of 20 °C. The reaction temperature in the literature was 10 °C, but this is below the melting point of the reagents and could lead to the formation of crystals in the IL. Crystals in the ionic liquid need to be avoid at all times to avoid crystallization of the ionic liquids. This is because ionic liquids have the tendency to supercool and solid reagent offer nuclei for crystallization [45]. This can be done by choosing a temperature above the melting point is highest for acetic acid (17 °C) and thus a temperature of 20 °C is chosen for the thermostatic bath.

A small excess of acid will be added in a dropwise manner to control the amount of heat generated by the reaction. The excess of acetic acid is selected since it has a lower boiling point than the 2-hydroxyethylamine which makes it easier to remove during the purification and it is used to make sure that all the 2-hydroethylamine is converted into PIL. Next, the IL is stirred for more or less 24 h. The purification is performed by vacuum drying at a temperature of 100 °C instead of at 60 °C [43] and for the duration of 6 to 8 hours instead of 24 hours [43]. Another difference is that methanol (Sigma-Aldrich, 99.8%) is added during the purification at 4 hours and at 6 hours. The methanol is added to facilitate the purifications since it aids the mass transfer to the gas phase. This method of purification will allow to remove unreacted reagents more easily because the vacuum (0.020 mbar) lowers its boiling point.

2.4. Literature search for production of bis-(2-hydroxyethyl) ammonium acetate (BHEAA) and Tris-(2-hydroxyethyl) ammonium acetate (THEAA)

2.4.1. Comparison of the different methods of synthesis described in the literature

The first synthesis method is the one described by *Kurnia et al.(2009)* [42]. This is exactly the same procedure as described for the synthesis of 2-HEAA. The PILs are synthesized by neutralizing the proper alkanolamine (Bis-(2-hidroxy-ethyl) amine [DEA] and tris-(2-hidroxy-ethyl) amine [TEA]) with acetic acid (Figure 47). The proper alkanolamine and the acetic acid were added to a three-necked round bottom flask. This flak is equipped with a reflux condenser, a magnetic stirrer and an inlet and outlet for N_2 gas. The reaction mixture was cooled with N_2 gas at a temperature between 5 °C and 10 °C. The mixture was then continuously stirred for 3 hours. Afterwards, the mixture was purified from unreacted reagents under an N_2 atmosphere at 50 °C for 24 to 36 hours. Another work by the same authors, *Kurnia et al. (2011)* [46], used the same synthesis method. Neither of the works mentioned why these conditions were selected for the synthesis and purification.

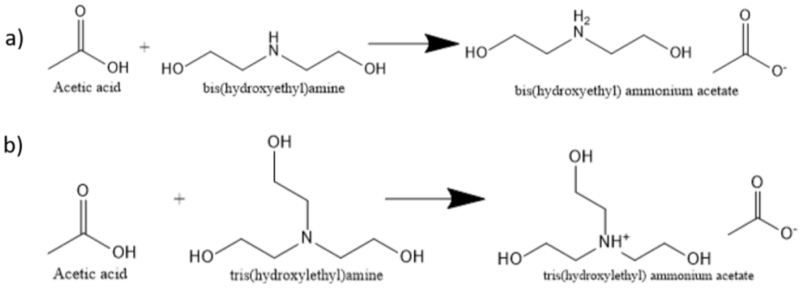

Figure 47: (a) Neutralization reaction of DEA with AA to synthesize BHEAA (b) Neutralization reaction of TEA with AA to synthesize THEAA

The second synthesis method is the one described by *Santos et al.(2016)* [47]. They added the proper alkanolamine in a three-necked round bottom flask and mounted this flask in an ice bath. The flask was equipped with a reflux condenser and an equimolar amount of acid was added dropwise to start the neutralization. During the reaction the temperature was kept at a temperature of 10 - 15 °C. After the addition, the mixture was kept stirring with a magnetic stirrer for 24 hours at a temperature of 27 °C. The purification of the PIL from unreacted reagents was achieved by drying the ILs overnight in roto-evaporator under vacuum conditions over phosphorous pentoxide. The control of the stirring temperature, the purification temperature, pressure or the amount of phosphorous pentoxide that is added in this work. There was no explanation for the conditions mentioned.

The final method is described by *Pinkert et al.(2010)* [48]. The beginning of the synthesis is similar to the method described by *Santos et al. (2016)* [47]. They added the proper alkanolamine first in the three-necked round bottom flask and then the acid in a dropwise manner to start the neutralization. The cooling of the flask is achieved by an ice bath. After the mixing of the acid and the alkanolamine, the mixture was kept stirring for 12 hours. Afterwards, the IL was stirred with molecular sieves for another 12 h to reduce the water content. This water could be an impurity in the reagents or a product of possible side reaction. The IL was then filtered through a nylon syringe filter under N_2 atmosphere to remove the molecular sieve residues. The exact temperature of reaction and purification were not mentioned. The reasons why these conditions were selected for the synthesis and the purification were not mentioned.

BHEAA and THEAA are, just like 2-HEAA, produced by a neutralization reaction with acetic acid, but DEA and TEA are used respectively instead of 2-hydroxyethylamine. The synthesis method of these PILs described in the literature is usually the same as 2-HEAA synthesis method, however there are some studies that use a slightly different approach, especially for the purification of the ionic liquids. A summary of the methods is given in Table 8.

Table 8: Summary of synthesis methods of BHEAA and THEAA found in the literature

Source	**Method of cooling**	**Stirring time**	**Method of purification**	**Purification temperature**	**Purification time**
Kurnia et al.(2009) [42], [46]	Flow of N_2 gas	3 h	Drying under N_2 atmosphere	100 °C	24 – 36 h
Santos et al.[47]	Ice bath	24 h	Roto-evaporation + drying in vacuum over P_2O_5	Not reported	overnight
Pinkert et al. [48]	Ice bath or oil bath	12 h	Molecular sieves + nylon syringe filter under N_2 atmosphere	Not reported	12 h

2.4.2. Selection of synthesis method and adjustments

For the synthesis of BHEAA and THEAA, we will use a similar method of synthesis as for the production of 2-HEAA. This being the neutralization of the alkanolamine by adding acetic acid in a dropwise manner to the three-necked round bottom flask. A small excess of acetic acid was used for the same reason as in section 9.3.2. The flask was cooled with a thermostatic bath at 30 °C for the synthesis of BHEAA and 25 °C for THEAA. This is again to avoid the formation of crystals in the ionic liquid, since the melting points for BHEAA and THEAA are 28 °C and 20.8 °C respectively. A small excess of acetic acid is used to ensure that the conversion of the alkanolamines are complete. After the addition of the acid the mixture was stirred for more or less 24 hours.

Vacuum drying is here too the preferred method to work with since it is simple method when compared to the other methods suggested in the literature. The vacuum drying is performed at the same temperature and pressure as the purification of 2-HEAA.

2.5. Literature search for the synthesis of L-Menthol-decanoic acid DES

2.5.1. Comparison of the different synthesis methods described in the literature

The first synthesis method of the L-menthol-decanoic acid DES is reported by *Ge et al. (2017)* [49]. They produced the DES by mixing the L-menthol and the decanoic acid (DA) in three different molar ratios (2:1, 1:1 and 1:2 [L-menthol:DA]) to investigate which ratio is the optimal ratio for the microextraction of benzophenone from aqueous samples. The synthesis was performed at 80 °C and magnetically stirred until a homogenous liquid was obtained. All batches were afterwards purified to remove impurities from the reagents by heating to 40 °C under a high vacuum for 5 days. The method reported in the work of *Florindo et al. (2014)* [50] was almost completely the same as the method described by *Ge* *et al.* for a molar ratio of 1:1. The only difference is that the purification is done in 4 days instead of 5. In both works, the reason why these conditions were selected was not mention.

The method described by *Verma et al. (2018)* [51] is similar to the previous one described. The L-menthol and the DA were mixed in a 1:1 molar ratio in a flat bottom flask. The mixture was heated to a temperature of 50 °C and stirred until a homogenous liquid was obtained. The purification was done via vacuum drying at a temperature of 60 °C for two days. The reason for the selection these conditions was not mentioned.

The DES produced by *Hümmer et al. (2018)* [52] followed a similar synthesis method. They mixed the components in a molar ratio of 65:35 (L-menthol:DA) and heated the mixture to a temperature 42 °C under continuous stirring. The reaction was complete when a homogenous liquid was obtained. There was no method of purification described in this work. An explanation for the selection of the conditions was not given in this work.

The final synthesis method is the one of *Martins et al.(2018)* [26]. They mixed the compounds in the same molar ratio as described by *Hümmer et al.*, but they experimentally determined the optimal molar ratio (eutectic point) by analyzing DESs with molar ratios. The resulting solid-liquid phase diagram shows that 65:35 (L-menthol:capric acid [other name for decanoic acid]) optimum molar ratio (Figure 48). The synthesis involved melting the components under stirring until a homogenous liquid was obtained. There is no mention of a reaction temperature or of a method of purification in this work.

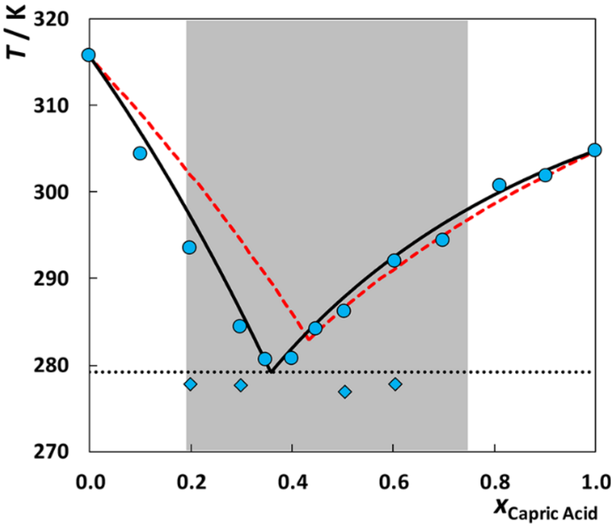

Figure 48: Experimentally obtained solid-phase liquid diagram for the l-menthol:decanoic acid DES obtained by Martins et al.(2018) [20]. The symbols represent the experimental data, the red line is the melting curve for an ideal liquid fase, the solid black line is the melting curve obtained by modelling with Pertubed Chain-statistical Associating Fluid Theory (PC-SAFT), The black dotted line indicates the eutect point generated by PC-SAFT and the grey area is the range of mixtures that are liquid at room temperature.

All studies produced this DES by mixing the components and heating them until a homogeneous liquid was obtained. However, the temperature and the molar ratio of both components was different. The purification is always vacuum drying, but the purification time and the temperature differed. A summary of the different studies is given in Table 9.

Table 9: Summary of synthesis methods of the L-menthol-decanoic acid DES found in the literature

Source	**Synthesis temperature**	**Mixing ratio* (L-Menthol:DA)**	**Purification temperature**	**Purification time**
Ge et al. [49]	80 °C	2:1	40 °C	5 days
	80 °C	1:1	40 °C	5 days
	80 °C	1:2	40 °C	5 days
Verma et al. [51]	50 °C	1:1	60 °C	2 days
Hümmer et al.[52]	42 °C	65:35	Not reported	Not reported
Florindo et al.[50]	80 °C	1:1	40 °C	4 days
Martins et al. [26]	Not reported	65:35	Not reported	Not reported

*: mixing ratios are mole ratios

2.5.2. Selection of synthesis method and adjustments

The DES based on L-menthol and decanoic acid will be produced like the literature suggest by heating the two components together in the same container under continuous stirring. The ratio suggested by *Martins et al. (2018)* [26] was chosen, since they were the only group that experimentally found the proper molar ratio to obtain a mixture at its eutectic point. The goal was to work with the 65:35 molar ratio, but an error was made and the molar ratio 35:65 was used instead. The results of this synthesis will be compared with a work that used a molar ratio of 1:2, since it is close to the used ratio. Starting temperature of the synthesis used was 40 °C and was slowly increased to 50 °C as soon as the components started to melt. After a couple of minutes at this temperature, the mixture became a liquid.

The estimation of the boiling points of the components in the vacuum was estimated in the same manner as for DHEAA and THEAA, with the formula of Clausis-Clapeyron (Equation 6) by using the fact that a liquid starts boiling when the vapor pressure is equal to the pressure of the space above the liquid, which is in this case 0.020 mbar.

$$\ln\left(\frac{P_{vap,2}}{P_{vap,1}}\right) = \frac{\Delta_{vap}H}{R} * \left(\frac{1}{T_{b,1}} - \frac{1}{T_{b,2}}\right) \qquad (6)$$

With P_{vap} the vapor pressure (mbar), $\Delta_{vap}H$ the vaporization enthalpy in kJ/mol, R the gas constant in kJ/(mol*K) and T_b the boiling point (K). The index 1 is at atmospheric conditions and index 2 is under the vacuum. The vaporization enthalpy for L-menthol and decanoic acid had a value of 56.6 kJ/mol and 65.73 kJ/mol respectively. This resulted in a boilin point around 4 °C for L-menthol and a boiling point of 38 °C for decanoic acid. So, the purification method that was chosen is vacuum drying at 60 °C for two days since this is the purification method that takes the least amount of time.

2.6. Production of 2-hydroxyethylammonium acetate

2.6.1. Chemicals

Acetic Acid (AA) (w ≥ 99,0%) was supplied by Sigma-Aldrich ®. 2-hydroxyethylamine (2-HEA) (w ≥ 99,50%) was also supplied by Sigma-Aldrich ®. The was no further purification performed on these chemicals.

Table 10: Description of the chemicals used in the synthesis of 2-HEAA

Chemical	**Supplier**	**State**	**Molecular weight ($g\cdot mol^{-1}$)**	**Purity (%w)**	**ρ ($g\cdot ml^{-1}$)***	**Melting point (°C)**	**Boiling point (°C)**
Acetic Acid (AA)	Sigma Aldrich	Liquid	60.052	≥99.0%	1.049	17	117 - 118
2-hidroxy-ethyl-amine (2-HEA)	Sigma Aldrich	Liquid	61.080	≥99.5%	1.020	10	169 - 170

*: The values given are for a temperature of 25 °C

2.6.2. Synthesis of 2-HEAA

To prepare a batch of 400 g (3.30 mol) of the ionic liquid, 201.68 g (3.30 mol) ethanol amine was put in a three necked round bottom flask. This flask was then mounted in a thermostatic bath (model RTE-200 from Nestlab) that is kept at 20 °C to remove the heat from the neutralization reaction. This flask was equipped with a dropping funnel to add the acid, a mechanical stirrer and a reflux condenser. The reflux condenser is used to condense the reactants that are evaporated by the heat from the reaction and the acetic acid that evaporates due to its volatility. These pieces were attached with joint clips to the flask. The entire setup is shown in Figure 49. After the setup is complete, 198.28 g (3.30 mol) acetic acid is added dropwise to the 2-hydroxyethylamine while continuously stirring. A mechanical stirrer is used since the use of a machinal stirrer is more efficient than a magnetic stirrer when working with viscous liquids. Some information about the final product is given in Table 11.

Table 11: Information about the PIL 2-HEAA

Chemical	**State**	**Molecular weight (g/mol)**	**Melting point (°C)**
2-hydroxyethyl ammonium acetate (2-HEAA)	Liquid	121.14	65 – 66

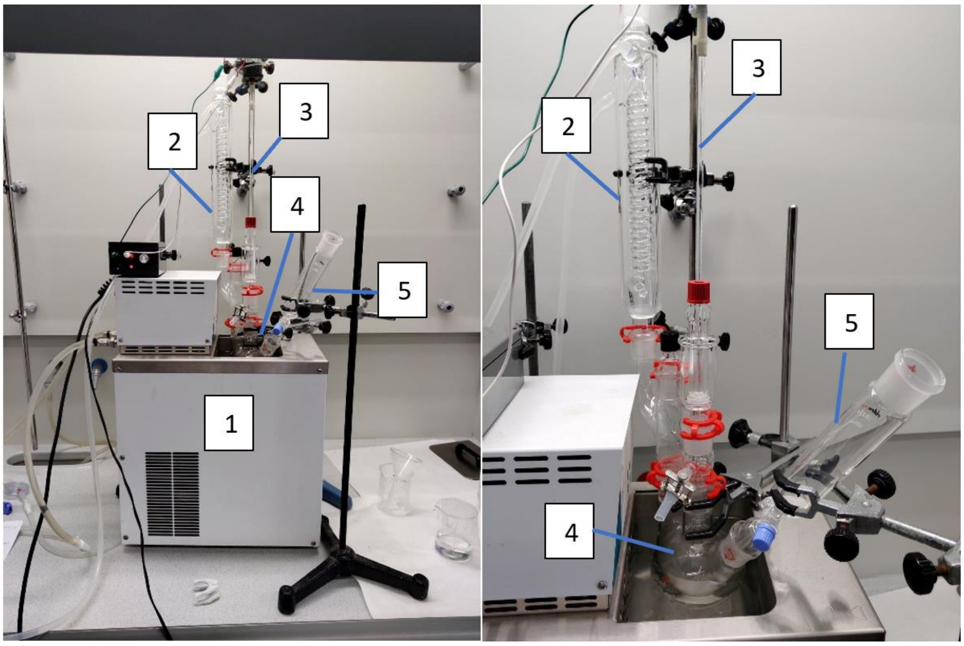

Figure 49: Setup for the synthesis of 2-hydroxyethylammonium acetate; (1) thermostatic bath, (2) reflux condenser, (3) mechanical stirrer, (4) three necked round bottom flask and (5) dropping funnel; (left) the entire setup and (right) a close-up of the flask.

Once all the acid is added, the mixture is stirred at 20 °C for a certain period of time to ensure a complete as possible conversion into the ionic liquid. In this case, it was chosen mixture stir for more or less 24 hours. Next, the ionic liquid was transferred with a funnel into a glass bottle with a screw cap (Figure 50).

It is important that the funnel is not submerged in the ionic liquid in the bottle, as can be seen in Figure 50. The surface of the funnel has a temperature that is lower than the melting point of the ionic liquid and will lead to the crystallization of the ionic liquid when submerged for too long. If this happens, the IL can be heated to 120 °C until it returns back to its liquid state.

Figure 50: Transferring of the ionic liquid

2.6.3. Measuring the completion of the reaction

The completion of the synthesis of the above-mentioned batches was followed up by measuring the refractive index of the ionic liquids with an Abbemat ® automatic refractometer (Figure 51) at 25 °C. The refractometer was calibrated with water. Before the start of the measurement, the lens must be completely covered with the ionic liquid, which required some droplets of the ionic liquid and the chamber is closed. It is important to check if there are no air bubbles in the liquids, because this can cause wrong measurements.

The measurement is based on the principle of internal reflection. When light goes from one medium to another, the angle of the beam of light changes due to refraction. When light travels from an optically denser medium to an optically less dense medium, there is a critical angle. If the incidence angle is greater than the critical angle, then the light will be completely reflected back into the medium and will not pass through the optically less dense medium.

Once the start button is pressed, a beam of light is sent though a prism onto the sample. If the angle at which the light hits the sample exceeds the critical angle, then the light is reflected onto a sensor. The lower the refractive index, the smaller the critical angle, the more light that hits the sensor. This means that the refractive index can be calculated by the ratio of the illuminated part of the sensor to part that is not illuminated.

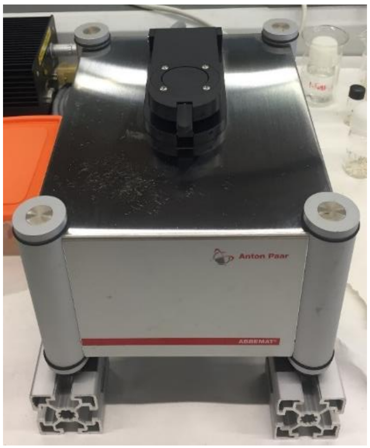

Figure 51: Anton Paar Abbemat ® automatic refractometer

After the measurement, the majority of the PIL is removed with a paper towel carefully, in a dabbing manner to avoid scratches on the lens. Then the lens is cleaned with acetone to remaining traces of the PIL. The lens is then again cleaned with a paper towel in a dabbing manner to remove most of the acetone (VWR Chemicals, 100%). Finally, the remaining traces of acetone are evaporated by blowing air over the lens. After cleaning, the lens is covered with a paper towel and the chamber with the lens is closed again. The reaction is considered complete when there is no trace of crystals (reagents or PIL) and when the refractive index had similar values to the ones reported in literature.

2.6.4. Purification of 2-HEAA

The PIL is transferred into an Erlenmeyer and remaining acetic acid was removed by vacuum drying. The system used for the drying consists of am Erlenmeyer 300 ml which is placed on a heating plate. This container is attached to an Edwards nXDS6iC vacuum pump with operates at 0,020 mbar (Figure 52). The ionic liquid is heated to 100°C continuously stirred with a magnetic stirrer while being purified. The purification is continued until the value of the refractive index remained constant within the fourth decimal, which was achieved after 6 to 8 hours of purifying. At 4 hours and the 6 hours, 4 ml methanol is added to the ionic liquid. This is done to facilitate the purification, since it improves the mass transfer to the gas phase. An important thing to mention, is that one batch of IL cannot fit entirely in the container. Therefore, is the reason why each batch was split in two before purification. If the vacuum would be broken, the liquid could be sucked into the pump which causes damage to the pump. To avoid this, a trap (the big bottle in the back on Figure 52) is installed as a security system so that if this a break in the vacuum were too happen, the liquid would be left in the trap and not into the pump. It has to be mentioned that this purification method takes a lot of time and that it requires a lot of energy, since it is a viscous liquid that needs to be continuously stirred and since the method requires vacuum conditions and relatively high temperatures. The purification considered complete when there is no more vapor visible above the PIL.

Figure 52: The system used for the vacuum drying; (left) The container and the heating plate and (right) the vacuum pump

2.7. Synthesis of bis-(2-hydroxyethyl) ammonium acetate and tris-(2-hydroxyethyl) ammonium acetate

2.7.1. Chemicals

Acetic Acid (AA) (w ≥ 99,0%) was supplied by Sigma-Aldrich ®. Bis-(2-hydroxyethyl) amine (DEA) (w ≥ 98%) and Tris-(2-hydroxyethyl) amine (TEA) (w ≥ 98%) were also supplied by Sigma-Aldrich ®. The was no further purification performed on these chemicals. The structures of these protic ionic liquids are given in Figure 53. Unfortunately, the synthesis of these PILs could not be performed due to the Corona outbreak.

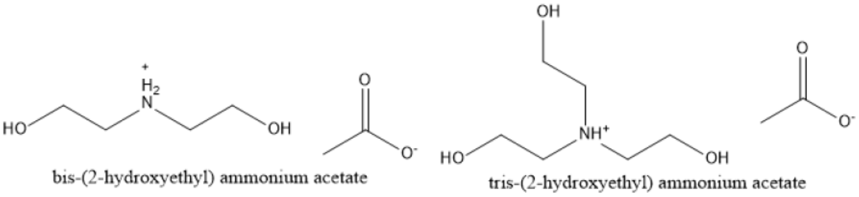

Figure 53: Structures of BHEAA (left) and THEAA (right)

Table 12: Chemicals used in the synthesis of BHEAA and THEAA

Chemical	**Supplier**	**State**	**Molecular weight ($g \cdot mol^{-1}$)**	**Purity (%w)**	**ρ ($g \cdot ml^{-1}$)***	**Melting point (°C)**	**Boiling point (°C)**
Acetic Acid (AA)	Sigma Aldrich	Liquid	60.052	≥99.0%	1.049	17	117 - 118
Bis-(2-hidroxy-ethyl) amine (DEA)	Sigma Aldrich	Liquid	105.14	≥98%	1.097	28	271.1
Tris-(2-hidroxy-ethyl) amine (TEA)	Sigma Aldrich	Liquid	149.19	≥98%	1.1242	20.5	335.4

*: The values given are for a temperature of 25 °C

Table 13: Information about the PILs BHEAA and THEAA

Chemical	**State**	**Molecular weight (g/mol)**	**Melting point (°C)**
Bis-(2-hydroxyethyl) ammonium acetate (BHEAA)	Liquid	160.20	-
Tris-(2-hydroxyethyl) ammonium acetate (THEAA)	Liquid	209.26	45

2.8. Production of the L-menthol and decanoic based DES

2.8.1. Chemicals

L-menthol (w ≥ 99%) was supplied by Sigma-Aldrich ®. Decanoic acid (DA) (w ≥ 98%) was also supplied by Sigma-Aldrich ®. No further purification was performed on these chemicals.

Table 14: Description of the chemicals used in the synthesis of the L-menthol and DA based DES

Chemical	**Supplier**	**State**	**Molecular weight ($g \cdot mol^{-1}$)**	**Purity (%w)**	**ρ ($g \cdot ml^{-1}$)***	**Melting point (°C)**	**Boiling point (°C)**
L-menthol	Sigma Aldrich	Solid	156.27	99	0.89	41 - 45	212
Decanoic Acid (DA)	Sigma Aldrich	Solid	172.26	98	0.893	27 - 32	269

*: The values given are for a temperature of 25 °C

2.8.2. Synthesis of the L-menthol and decanoic based DES

It was opted to produce 10 g of the DES to test the synthesis method. 3.282 g of L-menthol crystals and 6.718 g of decanoic acid crystals were added together in a glass container of 100 ml and this container is placed on the heating plate (IKA ® RCT basic). The temperature is gradually increased from the starting temperature 40 °C in steps of 2 °C until a temperature of 50 °C degrees is achieved. The temperature of the mixture is checked with a TP3001 digital thermometer. The magnetic stirrer is added once the mixture is almost completely liquid. The mixture is kept stirring at the temperature of 50 °C and at 260 rpm until a homogeneous, clear liquid is obtained.

To calculate the mass percentage, it was assumed that that 100 mol DES is produced with the wrong molar ratio. This mixture then consists of 65 mol of decanoic acid and 35 mol of L-menthol according to the mixing ratio. This allows the calculation of the mass of each component in the DES:

- Mass L-menthol: $35\ mol * 156.27 \frac{g}{mole} = 5469.45\ g$
- Mass decanoic acid: $65\ mol * 172.26 \frac{g}{mole} = 11196.9\ g$

The mass percentage of each component:

- L-menthol: $\frac{5469.45\ g}{5469.45\ g + 11196.9\ g} * 100\% = 32.82\ \%$ = 0.3282
- decanoic acid: $\frac{11196.9\ g}{5469.45\ g + 11196.9\ g} * 100\% = 61.18\ \%$ = 0.6118

This can then be used to calculate the necessary amounts of the reagents.

- L-menthol: $10\ g * 0.3282\ = 3.282\ g$
- Decanoic acid: $10\ g * 0.6718 = 6.718\ g$

2.8.3. Purification of the L-menthol and decanoic based DES

The produced batches of DES would have been purified with the same setup as for the purification of the 2-HEAA batches, but at 60 °C for the duration of 2 days. However, the purification was not performed due to the Corona outbreak.

2.9. Characterization and measurement of the thermophysical properties of the produced protic ionic liquids

The measured properties were the refractive index, water content, density and viscosity. The characterization was done via FT-IR, H-NMR and C-NMR.

2.9.1. Measurement of the refractive index

The refractive indexes of the PILs were measured before and after the purification to determine the influence of impurities on the properties of the PIL. The Abbemat ® automatic refractometer, that was used to follow the progress of the reaction, is used here to measure the refractive indexes.

2.9.2. Measurement of the water content

After purification, the water content of the batches of 2-HEAA were measured using a Karl-Fischer (KF) titrator model 787 KF Titrino supplied by Metrohm (Figure 55). The water in the PIL can be the result of impurities in the reagents, unwanted reactions or could be absorb from the atmosphere. The measurement is based on the Karl-Fischer reaction which is shown below in Figure 54. The alcohol, in this case methanol, reacts with SO_2 gas and a base (RN), which is in most cases imidazole or a primary amine, to form an intermediate alkylsulfite salt, which is oxidized by iodine to an alkylsulphate salt. The oxidization of this intermediate consumes water in a 1:1 ratio. Once the water is consumed, the device will detect the excess of iodine, which marks the end of the titration. The consumed amount of iodine is used to calculate the mass of water in the injected amount of ionic liquid [53].

$$CH_3OH + SO_2 + RN \rightarrow [RNH]SO_3CH_3 + H_2O + I_2 \rightarrow 2\ [RNH]I + [RNH]SO_4CH_3$$

Figure 54: Karl-Fischer reaction with methanol

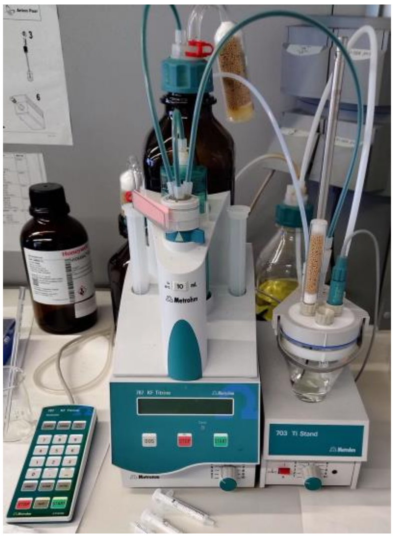

Figure 55: Metrohm Titrino ® Karl-Fischer titrator model 787 KF

The ionic liquid is drawn from the bottle with a syringe and the weight of this syringe is measured with an analytical balance. Next, a couple droplets of the ionic liquid are injected in the KF-titrator. Afterwards, the start button is pressed to start the measurement. Afterwards, the syringe is weighed with the same analytical balance and the difference between this weight and the original weight is calculated. On the measurement is done, this difference is entered in the KF-titrator and then the device calculates the w/w % of water of the injected protic ionic liquid. The chamber where the reaction occurs was drained after the measurement and was filled back up with methanol. Hydranal was used as an internal standard during the measurement and the measurement was conducted at room temperature.

2.9.3. Measurement of the density

The densities were measured with a density and sound velocity meter model DSA 5000M (Figure 56), which was supplied by Anton Paar.

Figure 56: Anton Paar DSA 5000M density and sound velocity meter

This type of density meter is an oscillating tube density meter. A 3 mL sample is taken from the bottle with the IL with a syringe and injected into the density meter. The U-tube is check for air bubbles, since the presence of air in the tube can gives wrong measurements. Next the measurement is started. The tube starts to oscillate, and the period (τ) of the oscillation (in seconds) is used to calculate the density Equation 7:

$$\rho = A * \tau^2 - B \qquad (7)$$

The coefficients *A* and *B* are equipment constants which are determined by calibrating the device. This calibration is in most cases performed with air and distilled water [54].

After the measurement, acetone is injected to purge the ionic liquid from the tube and, the build-in ventilator is turned on to evaporate the acetone (VWR Chemicals, 100%). The device is ready for the next measurement once the all the acetone is evaporated from the tube. The density meter has an internal camera that can be used to check if all the acetone in the U-tube is evaporated.

2.9.4. Measurement of the viscosity

The Viscosity was measured with an automatic rolling-ball viscometer (model AMVn) also supplied by Anton Paar (Figure 57). The appropriates capillary and ball need to be selected. Each ball and capillary have a specific viscosity range. If the wrong capillary and ball are chosen, then the ball will not fall to the bottom of the capillary or it will fall too fast and the device will give an error. In the literature various values for the viscosity of 2-HEAA were suggested (these are reported in section 3.4.), so the capillary and ball that were chosen are the ones that are suited for the lowest viscosity that was reported. This is a capillary with a diameter of 3 mm and a ball with diameter 2.5 mm (20 – 230 m Pa.s). If this measurement given an error, the viscosity of the PIL is too high for the capillary and ball and the measurement has to be repeated for another capillary and another ball [55].

Figure 57: Anton Paar AMVn automatic rolling-ball viscometer

A sample of the PIL is taken from the bottle with a syringe and injected in the capillary. The top of the capillary is sealed off and the ball is added at the bottom of the capillary. Once the bottom is also sealed, the capillary is placed in the device. The data of the appropriate capillary, type ball and angle of measurement are entered in the viscometer and then the start button is pushed. This puts the capillary at the desired angle, which is 60° in this case, so the measurement would not take too long, and the measurement starts. Once the measurement is completed, the PIL is removed from the capillary with acetone and the steel ball is captured, cleaned and reused.

2.9.5. Characterization of the ionic liquids

The ionic liquids were characterized with Fourier-Transform Infra-Red (FTIR) spectrometry and with H- and C- NMR spectroscopy. This was performed at the Central Service for the Support of Experimental Research (SCSIE) of the University of Valencia. The FTIR spectra were recorded with the Agilent Cary 630 FTIR spectrometer.

For the FT-IR spectrometer, it is important to check that there are no remaining traces of previous samples on the crystal in the spectrometer. These leftover traces could give wrong measurements. Next, the crystal is completely covered with the sample and the measurement is started. The spectrometer sends a range of different wavelengths of infra-red radiation through the sample and records how much of the radiation passes through the sample. After the measurement the crystal is cleaned using propanol (Emsure, 99.5%). In this work, the medium and high wavelengths are used (400 – 4000 cm^{-1}) for the recording of the FT-IR spectrum. There were 64 sample scans performed and 32 background scans with intervals of 1 cm^{-1}.

The principle behind NMR spectroscopy is based on the fact that some nuclei have a spin and that they are all electrically charged. A subatomic particle can be imagined as spinning around its own axis. In many atoms (such as C_{12}) the spins are paired against each other, which results in no overall spin. However there are some atoms (such as H_1 and C_{13}) that do possess an overall spin (I). This overall spin can have 2*I + 1 possible orientations and in the absence of a magnetic field these orientations have the same energy level. When a magnetic field is applied, the energy splits in levels, which each its own magnetic quantum number. According to the Boltzman distribution, the lower level contains more nuclei. The nuclei can be can transfer to a higher level by radiating them with electromagnetic waves with a frequency equal to their resonance frequency, which are usually radio waves. When the nuclei return to their original energy level, they send out radiation with their resonance frequency and this radiation can be measured by the NMR spectrometer. The resonance frequency is lowered by the surrounding electrons, which means that the same atom can have different frequencies depending on the surrounding atoms. It are these differences that allow a detailed determination of the structure of components [56].

The H-NMR and C-NMR spectra were recorded with a Bruker NMR spectrometer which operated at 500 MHz for the recording of the H-NMR spectrum and at 600 MHz for the recording of the C-NMR spectrum, both with deuterated methanol as solvent and a sensitivity of 10. The FT-IR, H-NMR and C-NMR spectra were recorded at a temperature between 20 and 25 °C. These spectra allow the detection and possible identification of the impurities and products of possible unwanted reactions.

2.10. Immiscibility of the DES with water

Due to the Corona outbreak there was no time to perform to characterize the DES with FT-IR, so it was decided to test the properties of the DES to see if the synthesis was successful. However, there was only time to test one of its properties, so the property that was chosen to focus on was the immiscibility with water, because it is the goal to use the DES as a solvent for the extraction of alcohols from aqueous mixtures and only a hand full of DES actually possesses this property. This was simply performed by putting a small amount of the synthesized DES in a test tube and adding a small amount of water to the DES. Next, the water and DES are mixed by shaking the test tube and the mixture was then left alone for a while. Afterwards, a visual observations was performed to check if the two original phases were present in the teat tube.

2.11. Method for the hydrolysis of end-of-life Poly (lactic acid)

The method for the chemical recycling of PLA with ILs is described by *Song et al.(2014)* and *McKeown et al.(2020)* [38], [57]. This method involved, mixing 2 g PLA with water in a ratio of 6:1 (m(H_2O):m(PLA)) and 1 g ionic liquid in an autoclave of 50 ml, which is equipped with a thermometer and a stirrer. The reaction, the mixture is heated to a 130 °C and kept at this temperature for a duration of 2 hours. Next, the unreacted PLA is removed via filtration and washed with small amounts of distilled water. The filtrate is weighted (w_1 in g) and a small amount of the filtrate is taken and also weighted (w_2 in g). This small amount of filtrate is titrated with sodium hydroxide (0.1 mol/L,VWR Chemicals) and phenolphthalein as indicator to calculate the conversion via Equation 8. The titration is repeated three times to obtain an average value [38], [57].

$$Conversion\ PLA = \frac{w_1 * C * V * M\ (LA)}{w_2 * w_3} * 100\ \% \qquad (8)$$

M(LA) is the molecular weight of lactic acid which is 90,08 g/mol; *C* (mol/l) and *V* (l) are the concentration and the volume of NaOH solution respectively; w_3 (g) is the theoretically produced mass of lactic acid when all the PLA is converted into lactic acid [43].

The above-described method is the method that will be used in this work. The main difference between the methods is that instead of an autoclave, pressure tubes of 100 ml, which are placed in aluminum jackets with a temperature sensor to check the temperature (Figure 58), are used in this work. This jacket was placed on an orbital shaker that shakes the tube at 120 rpm and heats it to the appropriate temperature (Figure 59). The used PLA is PLA 2003D grade from Natureworks, which is an extrusion-grade polylactide obtained from renewable resources.

Figure 58: Pressure tube (left) mounted in the aluminum jacket (right)

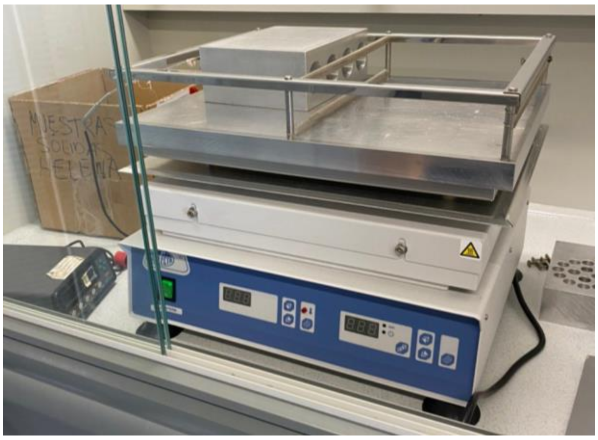

Figure 59: Orbital shaker used during the hydrolysis of PLA

3. Results and discussion

In this chapter, the results of the measurements that were performed on the PILs and the DES will be discussed. The results are discussed in the same order as they were mentioned in the section methods.

3.1. 2-hydroxyethyl ammonium acetate

3.1.1. Weighted amount of 2-hydroxyethylamine and acetic acid to synthesize 2-HEAA

All reagents were weighted with an Ohaus PA2202 Pioneer Precision Balance and the weighted amounts are given in Table 15. The calculations are illustrated for the production of 400 g ionic liquid.

- Ethanolamine: $\frac{400\ g}{121.14\frac{g}{mol}} * 61.08\frac{g}{mol} = 201.68$
- Acetic Acid: $\frac{400\ g}{121.14\frac{g}{mol}} * 60.05\frac{g}{mol} = 198.28\ g$

Table 15: Weighted amounts of AA and 2-HEA to produce the different batches of 2-HEAA

Batch	**$m_{2\text{-}HEA}$ (g)**	**m_{AA} (g)**
07/03/2019[a]	-	-
11/03/2019[a]	-	-
19/02/2020[b]	151.30	148.75
20/02/2020[c]	121.58	119.53
2/03/2020	201.69	198.30
4/03/2020	201.71	198.37

[a]: There are no data available for these batches, since they were already produced before the start of this project; [b]: Batches with the goal of producing 300 g of IL; [c]: The amount of 2-hydroxyethylamine in the laboratory was limited, so the weighted amounts are the amount to convert all the remaining 2-HEA into IL.

3.1.2. Refractive indexes (RI)

The refractive indexes of the 2-HEAA batches were measured before and after the purification to get an idea of the effect of the impurities on the properties. The refractive indexes of batches increase after the purification as can be seen in Table 16**Fout! Verwijzingsbron niet gevonden.** and the values do not differ significantly between batches.

The goal of the purification process was to remove volatile impurities which are present in the ionic liquid. These impurities are mostly the unreacted acetic acid, but also water absorbed from the atmosphere, as by-product from an unwanted reaction or a impurity in the reagents. During the purification, other by-products from unwanted reactions and other impurities from the reagents are also removed.

Table 16: Refractive indexes at 25 °C of the batches 2-HEAA before and after purification

Batch	RI before purification	RI index after purification	RI literature
07/03/2019	1.46699	1.47008	1.143682* [58]
11/03/2019	1.46838	1.46997	1.4711* [43]
19/02/2020	1.46810	1.47000	1.4754 [59]
20/02/2020	1.46940	1.47007	1.469 [60]
02/03/2020	1.46999	1.47010	-
04/03/2020	1.46992	1.47008	-

*:These measurement were performed at a temperature of 20 °C

The average value of the purified batches is 1.47009 with a standard deviation of ± 0.00006. This is close to the value reported by *Greaves et al.(2006)* [60] (1.469 ± 0.0005).What can also be noticed in Table 16, is that there are large differences between the literary values. These are most likely the result of a difference in water content or remaining species of the reagents.

The standard deviation and the coefficient of variation were also calculated using Equation 9 and Equation 10 respectively.

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}} \qquad (9)$$

$$coefficient\ of\ variation = \frac{s}{\bar{x}} * 100\% \qquad (10)$$

With *s* being the standard deviation, x_i the measured value, $\bar{x}$ the mean and *n* the number of measurements.

As can be seen in Table 17, the standard deviation after the purification is significantly smaller than the standard deviation before purification. This makes sense since before the purification, the compositions of the PILs are different due to different water and reagent contents . This results in bigger differences in the values of the refractive index and thus a larger standard deviation. After the purification all or almost all of the species that reduce the refractive index are removed. This results in smaller differences between the values of the refractive index of the batches and also in a smaller standard deviation.

Table 17: Determination of the standard deviation and the coefficient of variation on the measurement of the refractive indexes before and after purification

RI	Without purification	With purification 1	With purification 2
07/03/2019	1.46699	1.47003	1.47013
11/03/2019	1.46838	1.47001	1.46992
19/02/2020	1.46810	1.47004	1.47007
20/02/2020	1.46940	1.47008	1.47005
02/03/2020	1.46999	1.47009	1.47011
04/03/2020	1.46992	1.47004	1.47012
Arithmetic mean	1.46878	1.47009	
Standard deviation	0.00118	0.00006	
Coefficient of variation (%)	0.08034	0.00408	

3.1.3. Thermophysical properties

The densities and the water contents of the 4 purified batches of 2-HEAA are shown Table 18**Fout! Verwijzingsbron niet gevonden.**. The most notable feature is that the density of the first batch is a lot lower than the density of all other batch, while the lowest density was expected for the third batch since this it has the highest water content. The reason why this density of the third batch is higher than expected might be the presence of by-products in the ionic liquid. These by-products can be from the N-(2-hydroxyethyl) acetamide from the condensation reaction or carbamates and/or oxazolidinone-2 that are formed by the reaction of ethanolamine with CO_2 from the atmosphere (Figure 60**Fout! Verwijzingsbron niet gevonden.** and Figure 61**Fout! Verwijzingsbron niet gevonden.**) [61],[62]. The presence can be confirmed by analyzing the H-NMR or in the C-NMR spectra. The discussion of these spectra is done in sections 3.1.5 and 3.1.6., but these spectra do not confirm the presence of these components. This leads to the conclusion that these compounds are not relevant impurities. All of these ionic liquids can still be considered pure, since the amount of water present in all of these ILs is below 1%.

Table 18: Measured and literature values for the water content, densities and viscosities of the 2-HEAA

Batch	Water content (w/w %)	ρ (g/cm^3)^b	Water content lit.^{a} (w/w%)	ρ lit. (g/cm^3) ^{b}	μ lit. (mPa.s)^c
11/03/2019	0.524342	1.153869	-	1.151 [25]	-
20/02/2020	0.240483	1.155057	-	1.1559 [43]	448.0 [43]
02/03/2020	0.838986	1.154872	0.0158 [42]	1.14866 [42]	313.15 [42]
04/03/2020	0.331818	1.154602	-	-	640 [2]
-	-	-	-	-	252 [63]

[a]: lit. is an abbreviation to indicate values mentioned in the literature; [b]: at 20 °C; [c]: at 25 °C

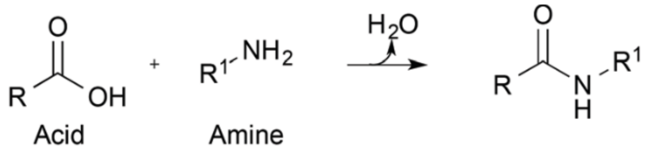

Figure 60: Reaction of a carboxylic acid and an amine to an amide [64]

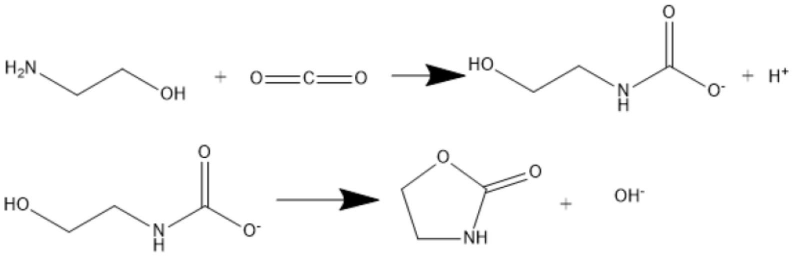

Figure 61: Reaction of 2-hydroxyethylamine into a carbamate and oxazolidinone-2

The value of the density is on average 1.154844 ± 0.000028 g/cm^3. When comparing this value to the values reported in literature, then it can be noticed the one measured in this study is closest to the value reported by *Hosseini et al.(2019)* (1.1559 ± 0.000021 g/cm^3)[65]. The values reported by *Pinkert et al.(2010)* [25] and *Kurnia et al.(2008)* [42] show significantly larger differences.

The standard deviation is calculated using the same equation that was used to determine the standard deviation of the RI-measurements (Equation 9). This value is 0.000522 g/cm^3 and is significantly larger than the one reported by *Hosseini et al. (2019)* [65]. This is the result of the density of batch 11/03/2019 that is a lot lower than the values of the other densities and since there are only four measurements done, this heavily influences the standard deviation.

Table 19: Calculation of the standard deviation of the measured values of the density.

Batch	**Density (g/cm^3)**
11/03/2019	1.153869
20/02/2020	1.155057
02/03/2020	1.154872
04/03/2020	1.154602
Arithmetic mean	1.154600
Standard deviation	0.000522
Coefficient of variation (%)	0.045203

The mean and the standard deviation have values of 1.154844 g/cm^3 and 0.00023 g/cm^3 respectively if this measurement is not taken into consideration. This new standard deviation is significantly smaller, than the one taking batch 11/03/2019 into consideration.

It is possible to determine if the value for batch 11/03/2019 is an outlier. This can be done by using Equation 11.

$$\lfloor x - \bar{x}^{*} \rfloor > 3 * s^{*} \qquad (11)$$

With x the value of the possible outlier, $\bar{x}^*$ the mean of the other measurements and s^* the standard deviation of the other measurements. $\bar{x}^*$ and the s^* have values of 1.154844 g/cm^3 and 0.00023 g/cm^3 respectively. This new standard deviation is significantly smaller than the one taking batch 11/03/2019 into consideration. Besides this, the result of the right side of Equation 13 is 0.00097 g/cm^3, which is larger than 0.00069 g/cm^3 (three times s*). This results in the conclusion that the value for batch 11/03/2019 is an outlier and that I can be left out. The new values for the mean and the standard deviation are 1.154844 g/cm^3 and 0.00023 g/cm^3 respectively. This new standard deviation is similar to the one reported by *Hosseini et al. (2019)* [65] (0.000021 g/cm^3).

There are no measured values for the viscosity, since the selected capillary and ball were not appropriate for the viscosity of the ionic liquid. The viscosity of the produced batches was higher than the lowest recorded value, so a capillary with a diameter of 4 mm and a ball with a diameter of 3 mm had to be used instead, since the measuring range for this equipment 80 – 2500 mPa·s is [55]. However, the measurements could not be continued due to the absence of the correct capillary in the laboratory and the Corona outbreak. Just like with density, there are large differences between the values reported in the literature.

The measured values of the density are similar to some of the values reported in the literature, but there are large discrepancies between the values for the density and the viscosity reported in the literature. These discrepancies are most likely caused by the differences in water content, purity or/and the experimental method used to determine the properties. Due to these discrepancies it is not possible to determine if the synthesis was successful based on the values of the thermophysical properties alone. The FT-IR and the NMR spectra can be used to determine if the synthesis was successful without a margin of error.

3.1.4. Fourier Transform Infra-Red spectrum

FTIR spectroscopy was used to further characterize the synthetized PILs. This result was then compared with the spectrum recorded by *Rocha et al.(2017)* [59], since this is the FT-IR spectrum recorded for the same PIL. Both spectra are shown in Figure 62. It is clear that the transmittances of the wavelengths of both spectra are similar:

- Between 2500 and 3500 cm^{-1} (a), which is characteristic for amine structures. The OH, CH_3 and CH_2 stretching vibrations are also incorporated in this band.
- Between 1500 and 1800 cm^{-1} (b), which is most likely caused by the O=C- stretching and N-H- curvature vibrations.
- Between 800 and 1500 cm^{-1}, most likely caused by the C-O- and C-N- bonds. With the band between 1500 and 1200 cm^{-1} (c) the result of C-O stretching and the band between 1200 and 800 cm^{-1} (d) the result of C-N stretching.

The works published by *Rocha et al.(2017)* [59] and by *Verberckmoes and Stals (2018)* [66] were used to identify the bands. These bands in the spectra were expected for the PIL 2-HEAA and give an indication that the synthesis was successful. There is one band between 800 – 500 cm^{-1} in the spectrum recorded in this work that might indicate the presence of some sort of impurity. This impurity is most likely a compound with a disubstituted cis-double bond, since these cause bending vibrations that cause a band between 800 and 680 cm^{-1}, or a monosubstituted aromatic compound, since these give strong absorptions at ± 680 cm^{-1} and at ± 750 cm^{-1}. The H- and C-NMR can give more information about these possible impurities. Besides this one band, the spectra show a significant resemblance which indicates that the synthesis was successful.

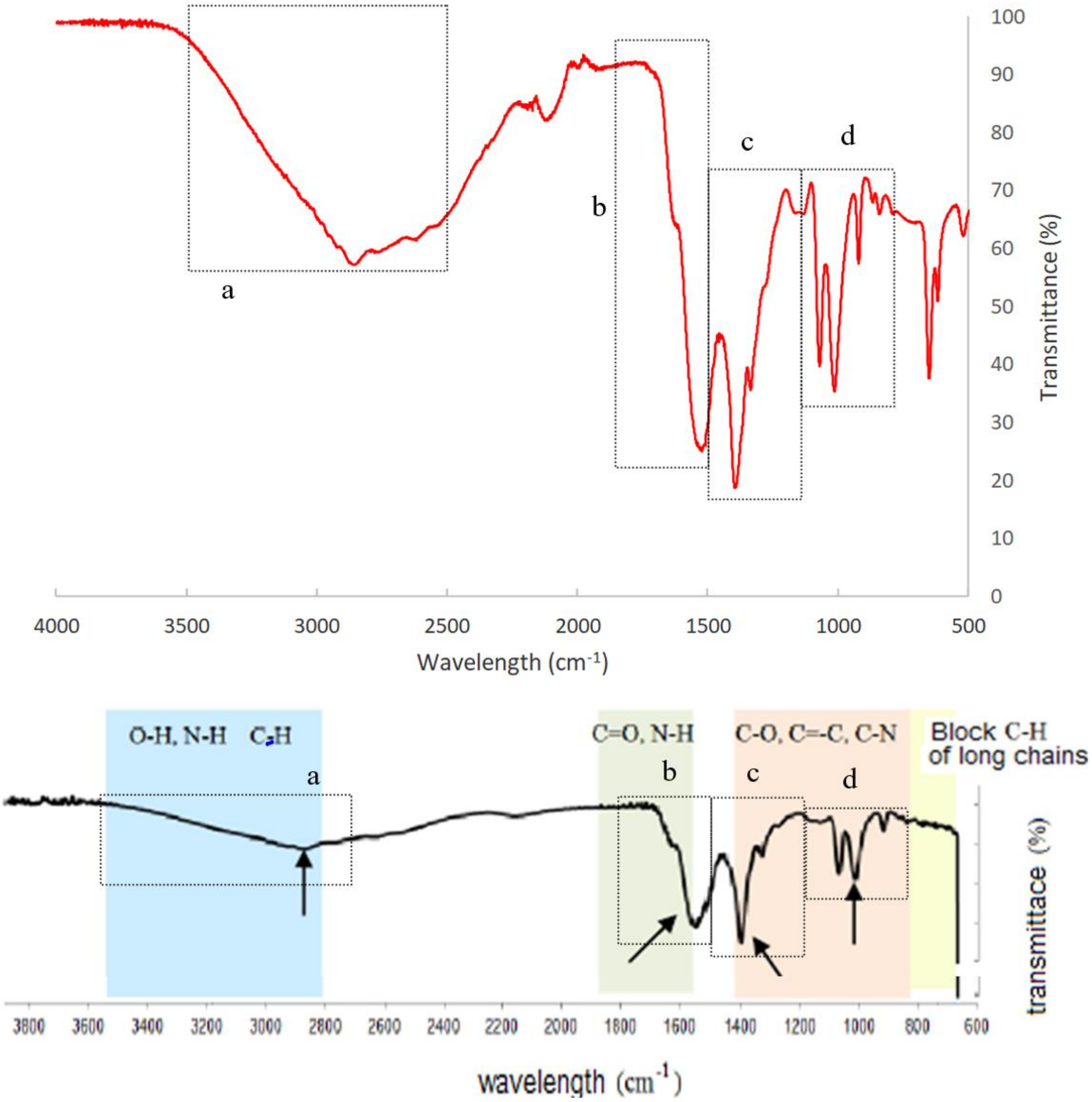

Figure 62: FT-IR spectrum of the PIL 2-HEAA synthesized in this study (top) and the one reported by Rocha et al. [45] (bottom)

3.1.5. Proton Nuclear Magnetic Resonance Spectrum

The recorded H-NMR spectrum and that of *Rocha et al. (2017)* [59] are shown in Figure 63. Both were spectra are for the PIL 2-HEAA, but the solvent that used is different. This is deuterated methanol for this work and deuterated chloroform for *Rocha et al. (2017)* [59]. The first three peaks recorded (starting from the right) are the same for both spectra:

- At δ = ± 2 ppm: This peak is most likely caused by the hydrogens on the methyl groups.
- At δ = ± 3 ppm: This peak is most likely caused by the hydrogens in the methylene group next to the ammonium group.
- At δ = ± 3.8 ppm: This peak is most likely caused by the hydrogen in methylene group next to the hydroxyl group.

The next peaks are different for both spectra. The n peak at δ = 5.4 ppm is most likely caused by the hydrogen in the hydroxyl group, but this hydrogen is strongly deshielded due to the formation of hydrogen bonds with the deuterated methanol. The peaks at δ = 7.2 ppm and δ = 7.6 ppm in the spectrum recorded by *Rocha et al.* [59] are most likely the result of the deuterium in the deuterated chloroform that is used as solvent. The works published by *Rocha et al.(2017)* [59] and by *Verberckmoes and Stals (2018)* [66] were used to identify the peaks. There are no other peaks besides the peaks of the PIL 2-HEAA and the solvent peaks in both spectra. This leads to the conclusion that there are no significant impurities and that the synthesis of the PIL can be considered successful.

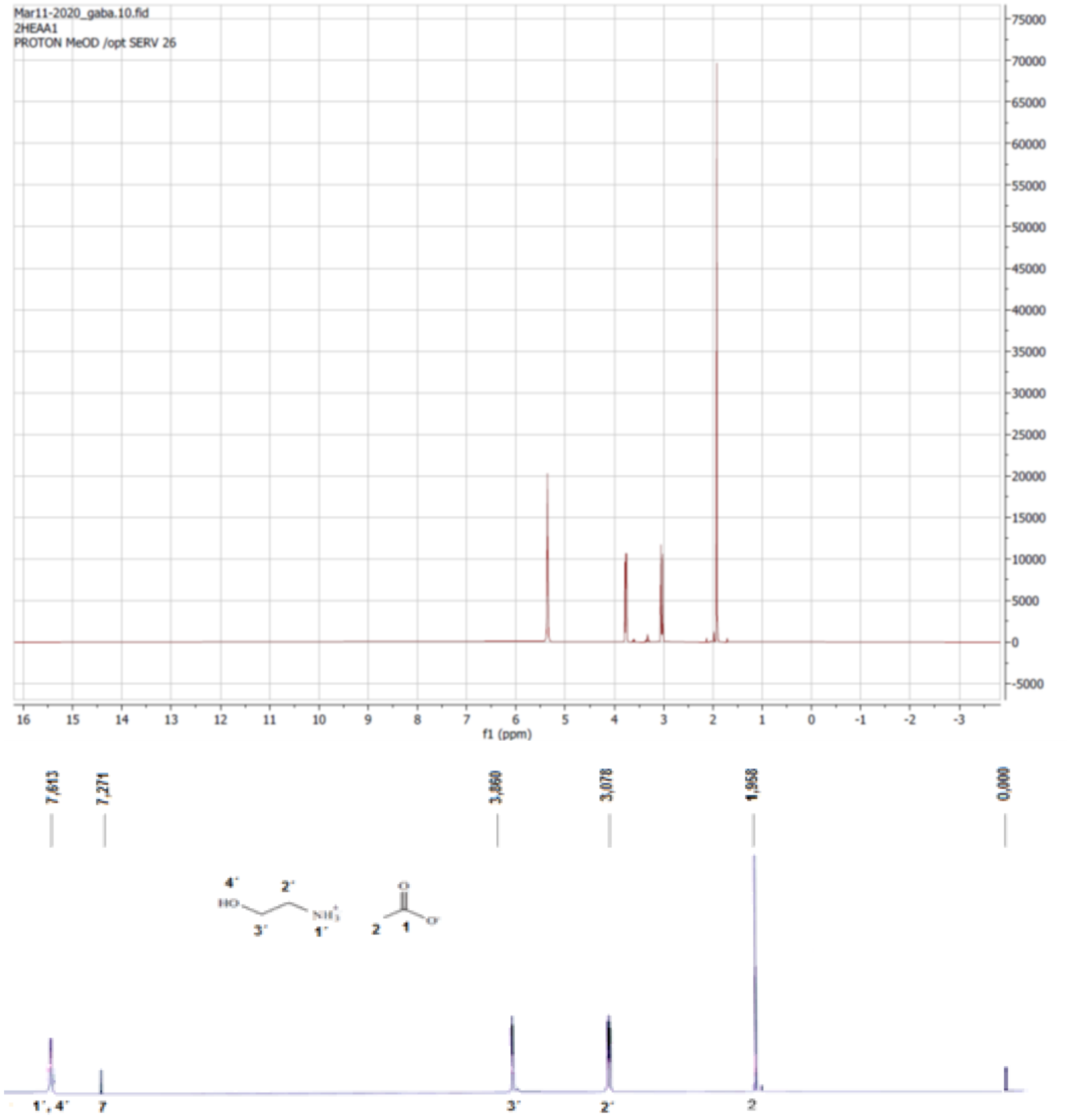

Figure 63: H-NMR spectrum of the PIL 2-HEAA synthesized in this study (top) and the one reported by Rocha et al. [45] (bottom)

3.1.6. Carbon Nuclear Magnetic Resonance Spectrum

Finally, C-NMR was also used to characterize the produced 2-HEAA. The recorded spectrum and the spectrum of by *Rocha et al. (2017)* [59] are shown in Figure 64. The recorded spectrum was compared. All the peaks are the same for both spectra, which was expected since both spectra are recorded for 2-HEAA with deuterated methanol as solvent. The peaks are summed up below:

- At δ = 24.45 ppm: This peak is the result of the carbon in the methyl group in the acetate ion.
- At δ = 42.81 ppm: This peak is caused by the carbon in the methylene group next to the ammonium group.
- At δ = ± 49 ppm: This is the peak resulting from the carbon in the solvent.
- At δ = 59.20 ppm: This peak is the result of the methylene carbon next to the hydroxyl group.
- At δ = 180.33 ppm: This peak is caused by the carbon from the carboxyl group.

The study published by *Rocha et al.(2017)* [59] was used to identify the peaks. There are no other peaks besides the peaks of the PIL 2-HEAA and the solvent peak that would indicate the presence of other components. Together with the fact that the spectra show a significant resemblance, indicate that the synthesis was successful.

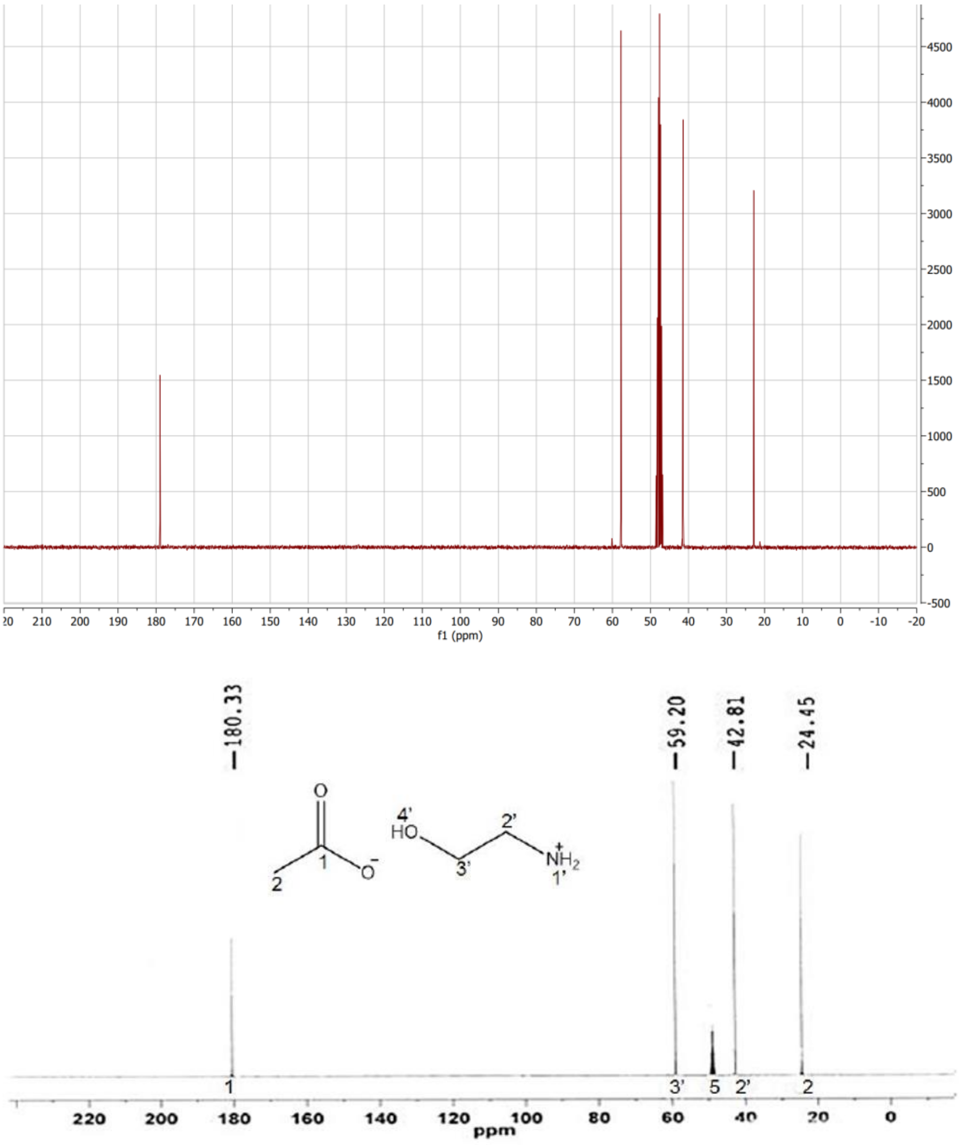

Figure 64: C-NMR spectrum of the PIL 2-HEAA synthesized in this study (top) and the one reported by Rocha et al. [45] (bottom)

3.2. L-menthol:Decanoic acid DES

3.2.1. Weighted amount of L-menthol and decanoic acid to synthesize the desired DES

Both L-menthol and decanoic acid (Figure 65) were weighted using a Mettler Toledo ® XSEao5 DualRange analytical balance. The weighted amounts are given in Table 20. The final molar ratio obtained with the weighted chemicals is 34.4:65.6 (L-menthol:Decanoic acid).

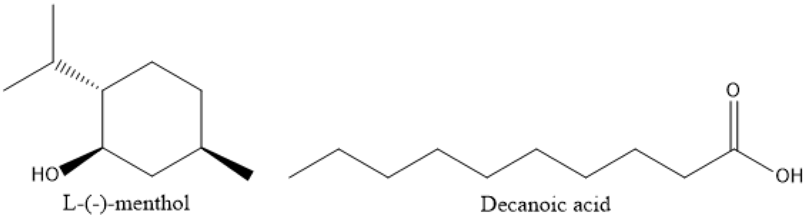

Figure 65: Structure of L-menthol (left) and decanoic acid (right)

Table 20: Weighted amounts of L-menthol and DA to synthesize the DES

Batch	**$m_{L\text{-}menthol}$ (g)**	**$m_{decanoic\ acid}$ (g)**
27/02/2020	3.2846	6.8962

3.2.2. Quality of the synthesized DES

A deep eutectic solvent is different from an ionic liquid and can be made with different proportions of the reagents. However, the ideal properties are achieved at the eutectic composition. Ideal properties are not expected for the DES produced in this work, since the molar ratios were reversed (35:65 instead of 65:35 [L-menthol:decanoic acid]) , but it was still expected that the synthesized DES showed the expected properties. Due to the Corona outbreak there was no time to test all properties of the synthesized DES, so the property that was chosen to focus on was the immiscibility with water, because it is the goal to use the DES as a solvent for the extraction of alcohols from aqueous mixtures and only a hand full of DES actually possesses this property. The synthesized DES indeed seems to be partially or fully immiscible with water as can be seen in Figure 66. Together with the fact that the DES was liquid at room temperature, this gives an indication that synthesis was successful and it is only the mixing ratios need to be changed for future research after the Corona outbreak.

Figure 66: Immiscibility of the produced DES with water

3.2.3. FT-IR spectrum and properties of the DES reported in the literature

One of the goals was to characterize the DES, but unfortunately this was not possible due to the Corona outbreak. Even though the data reported in the literature for the future comparison are given in this section. Like mentioned in section 2.5.2., the literary spectra for the DES with composition (1:2) reported by *Zarei et al.(2018)* (Figure 67) can be used for the comparison to check if the synthesis itself is successful since this composition is closest to the composition of the synthesized DES.

The properties reported by *Martins et al.(2018)* [26] are given in Table 21 for comparison in future studies. It must be noted that the reported value of for the DES with the desired composition of 65:35. Even with the similar mixing ratio as the one for which the FT-IR spectrum was recorded, there might still be some differences that will make it difficult to confirm the method of synthesis. In the end, it is advised to synthesis a batch with the same ratio as in the work of *Zarei et al.* [16], since the synthesis is easy and cheap and since this batch can then be used to confirm the method of synthesis with 100% certainty.

Table 21: Values found in the literature for the properties of the L-menthol:DA (65:35) DES

Mixing ratio (L-menthol:DA)	**Refractive index**	**Water content (w/w%)**	**Density at 20 °C (g*cm^{-1})**	**Viscosity at 25 °C (mPa.s)**
65:35	-	-	0.9002	18.85

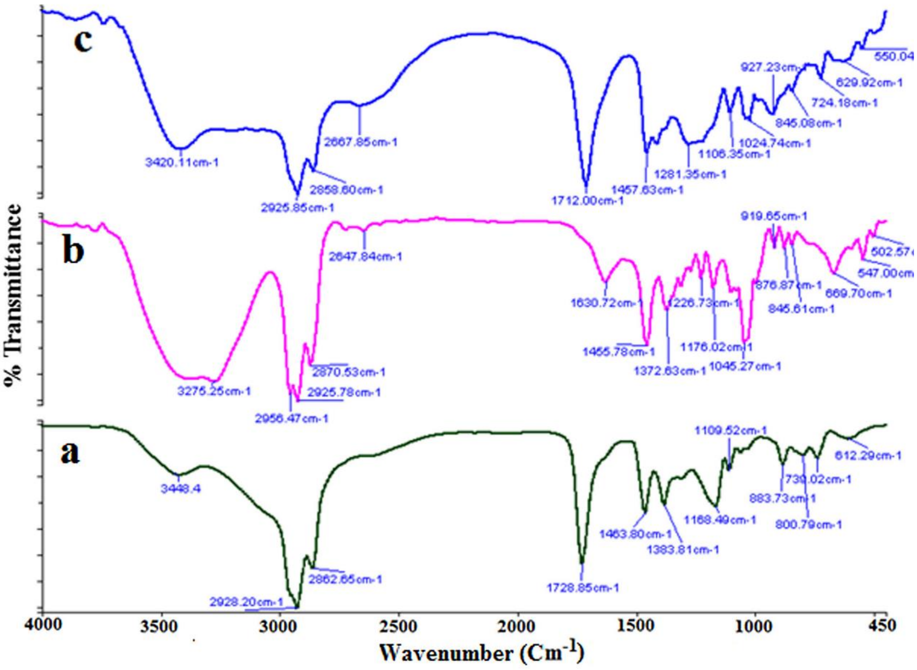

Figure 67: FT-IR spectra of (a) Decanoic acid, (b) L-menthol and (c) L-menthol:DA DES (1:2) reported by Zarei et al. [15]

3.3. Hydrolysis of PLA

First, the hydrolysis of PLA was investigated by another student of the University of Valencia at the conditions that were described in section 2.11., but with one of the ionic liquids described by *Song et al.(2014)* [57], [Emim][OAc], but this reaction did not give good results. A conversion around 90% was expected for this ionic liquid since this was the recovery described in *Song et al.(2014)* [57]. However, after performing the experiment about a third of the initial PLA was still present in the pressure tube, which indicates that the 90.86 % conversion was not achieved. In the next experiment, the particle diameter of the PLA was reduced from 5 mm to 0.5 mm, but the conditions and the ratios were the same. This gave the same results as the prior experiment, which are both shown in Figure 68.

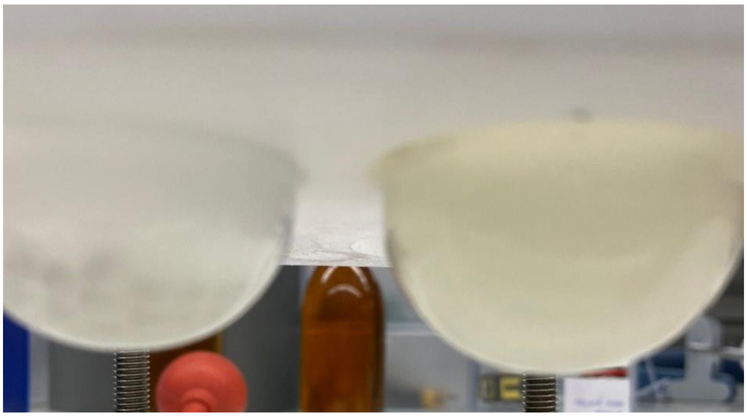

Figure 68: PLA remaining after the hydrolysis with particles with a diameter of 5 mm (left) and with diameter 0.5 mm (right).

In another experiment, the amount of PLA was reduced to 1 g and the reaction time was gradually increased until there was no PLA observed. All other conditions and the mass ratio water/PLA/IL (6:1:0.5) were the same. After increasing the reaction time to 5.5 hours, there was almost no more PLA visible in the mixture (Figure 69). At this reaction time a conversion of more than 100%, 118% to be precise, was achieved. After opening the pressure tube, the mixture inside the tube immediately smelled like of acetic acid. This led to the assumption that the ionic liquid decomposed during the reaction into 1-ethyl-3-methylimidazole and acetic acid, which was not expected to happen. This would also explain the value for the recuperation since the acetic acid interferes with the titration.

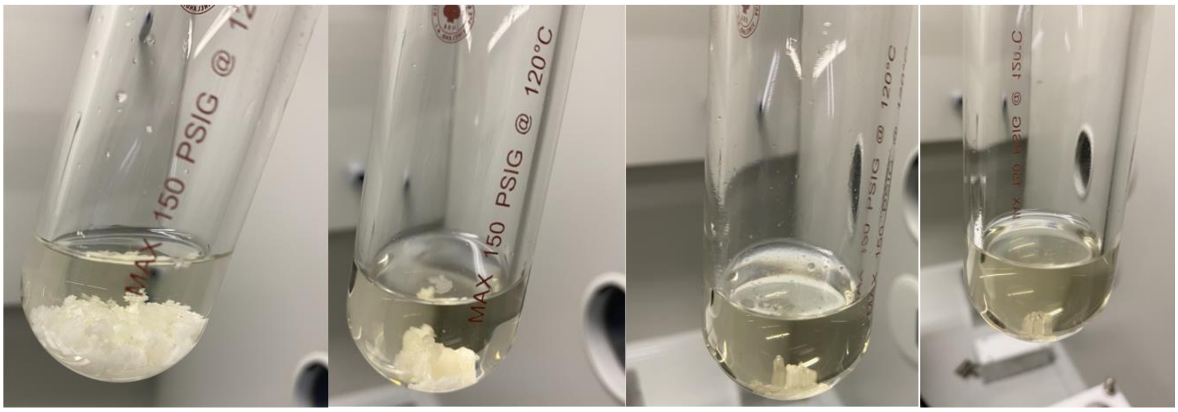

Figure 69: The results for the hydrolysis of PLA with increasing reaction time (left to right)

Next, two pressure tubes were prepared: one with only water and IL with the mass ratio (6:0.5) and one with water, PLA and IL with the mass ratio (6:1:0.5). The decomposition of the IL was checked via titration of the mixture in the first tube with the NaOH solution. The titration of the first tube was then used as correction for the titration of the mixture from the latter tube. After the correction, the reaction at 130 °C for 5.5 hours with the mass ratio of water/PLA/IL (6:1:0.5) gave a conversion of 95.56%.

After the laboratory was reopened due to relaxation of the Corona measures, the hydrolysis of PLA was performed with the synthesized 2-HEAA as catalyst and with the following parameters: A mass ratio of 6:1:0.5 for water/PLA (0.5 mm)/IL, a temperature of 130 °C and a reaction time of 5.5 hours. The weighed amounts for the hydrolysis are given in Table 22.

Table 22:Weighed amounts of reagents for the hydrolysis of PLA with 2-HEAA as catalyst.

Pressure tube	**m_{water} (g)**	**m_{PLA} (g)**	**mPIL (g)**
Correction tube	6.0200	1.0000	0.5100
Hydrolysis tube	6.0100	N.A.	0.5000

N.A.: Not applicable

The conversion was calculated using Equation 8 from section and the results are reported in Table 23. w_3 has for all tubes a value of 1.0000 g. The calculation of the conversion is illustrated for the first hydrolysis tube.

$$Conversion\ PLA = \frac{16.6927\ g * 0.1\ \frac{mol}{L} * 0.0131\ L * 90.08 \frac{g}{mol}}{2.0194\ g *\ 1.0000\ g} * 100\% =\ 97.54\ \%$$

Table 23: Results of the PLA hydrolysis with 2-HEAA as catalyst.

Test tube	**Titration**	**w_1 (g)**	**w_2 (g)**	**V_{NaOH} (mL)**	**$V_{NaOH,\ Corrected}$ (mL)**	**Conversion (%)**
Hydrolysis tube	1	16.6927	2.0194	14.9	13.1	97.54
	2		2.0254	15.0	13.2	97.87
Correction tube	1	16.6715	2.0153	1.8	N.A.	N.A.

N.A.: Not applicable

The average conversion for the hydrolysis of PLA with 2-HEAA as catalyst is 97.71 %. The best result reported by *Song et al.(2014)* [57] was achieved for the AIL 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) at 130 °C, a mass ratio of 12:2:1 (water/PLA/IL) and a rection time of 2 hours. This AIL had a conversion of 93.93%, which is a bit less than the conversion obtained in this work for 2-HEAA, but it is important to notice that the reaction time of for the AIL was a lot shorter. If the hydrolysis with [Bmim][OAc] was given the same reaction time as for 2-HEAA (5.5 hours), the conversion might be similar or even better than the one obtained by using 2-HEAA. This makes it difficult to decide which of these two ionic liquid is better for the hydrolysis of PLA.

The conversion with 2-HEAA is slightly better than the 95.56% that was achieved for hydrolysis with [Emim][OAc] as catalyst, but advantage that PILs have over AILs is that there are generally considered to be greener and that their production cost is smaller. For this reason, it is advised to use the PIL for the hydrolysis instead of the AIL, even though the conversion are similar.

4. Conclusion

In the current work, the methods to synthesize the 2-hyrdoxyethyl ammonium acetate, bis-(2-hydroxyethyl) ammonium acetate, tris-(2-hydroxyethyl) ammonium acetate protic ionic liquids and the L-menthol-decanoic acid deep eutectic solvent from literature were studied and compared with each other. The most appropriate method was subsequently selected and adjustments were made. These adjusted methods of synthesis were then used for the synthesis of the protic ionic liquid 2-hyrdoxyethyl ammonium acetate and deep eutectic solvent.

For the protic ionic liquid 2-hyrdoxyethyl ammonium acetate, all synthesis methods involved the neutralization reaction of 2-hydroxyethyl amine with acetic acid. The 2-hydroxyethyl amine was first loaded into a three-necked round bottom flask. The flask is subsequently mounted in a thermostatic bath for cooling, which is kept at 20 °C to avoid crystallization of the protic ionic liquid. The flask is then equipped with a reflux condenser to condense the reagents in the gas phase. The reaction is started by adding the acid in a dropwise manner. This is done in a small excess of the acid to ensure full conversion. After the addition, the mixture is kept stirring overnight to further ensure the full conversion. The purification was performmed via vacuum drying at 100 °C for 6 to 8 hours with methanol vapor entrainment at 4 and 6 hours to increase the efficiency of the purification.

The most appropriate method of synthesis for bis-(2-hydroxyethyl) ammonium acetate and for tris-(2-hydroxyethyl) ammonium acetate is similar to the one of 2-hyrdoxyethyl ammonium acetate, but respectively with the neutralization of bis-(2-hydroxyethyl)amine and tris-(2-hydroxyethyl)amine with acetic acid. The only difference is the reaction temperature (30 °C for bis-(2-hydroxyethyl) ammonium acetate and 25 °C for 2-hyrdoxyethyl ammonium acetate) to prevent the ionic liquid from crystalizing. The purification is performed in the same manner as for 2-hyrdoxyethyl ammonium acetate.

The most optimal method for the synthesis of the L-menthol:decanic acid deep eutectic solvent is by mixing L-menthol and decanoic acid in a molar ratio of 65:35 and then heating the mixtures until a homogenous liquid is obtained like *Martins et al.(2018)*[26] suggests. However, due to an error, the wrong molar ratio of 35:65 was used instead. The temperature was then gradually increased for 40 °C in steps of 2 °C until 50 °C was achieved. Once both compounds were in a liquid state, a magnetic stirrer was added to the mixture and it was kept stirring at 260 rpm until a homogenous liquid was obtained. Afterwards, the DES would have been purified via vacuum drying for 2 days at a temperature of 60 °C as suggested by *Verma et al (2018)*[51]. Unfortunately, the purification could not be performed due to the Corona outbreak.

The refractive indexes, the densities and the viscosities of the produced batches of 2-hydroxyethyl ammonium acetate were also measured. The refractive indexes and the densities of the batches showed no significant variation between each other. The value of the refractive index was on average 1.47009 ± 0.00006 and the average value of the density 1.54844 ± 0.000023 g/cm^3. There are no measurements for the viscosity of this protic ionic liquid, since the appropriate equipment to measure it was not available in the laboratory. The measured values were also compared with the values reported in the literature. The measured values are similar to some of the values reported in the literature, but there are large discrepancies between the values reported in the literature. Due to these discrepancies it is not possible to determine if the synthesis was successful based on the values of the thermophysical properties alone. The FT-IR and the NMR spectra can be used to determine if the synthesis was successful without a margin of error.

The characterization of 2-hydroxyethyl ammonium acetate via FT-IR, H-NMR and C-NMR was compared with the spectra found in the literature to check the synthesis. All three spectra of 2-hydroxyethyl ammonium acetate showed a significant resemblance with the spectra found in the literature. There was only a small difference in the H-NMR spectrum, which was most likely the effect of the solvents that were used to dissolve the protic ionic liquid. The resemblance between these spectra leads to the conclusion that the synthesis was successful.

Confirmation of the synthesis method of the deep eutectic solvent was done by testing its immiscibility with water. The deep eutectic solvent did in fact show this property, which led to the assumption that the synthesis method was correct and promising for the future synthesis of deep eutectic solvents with other mixing ratios. In future research the solvent will be characterized with FT-IR.

The hydrolysis of poly (lactic acid) was tested with one of the aprotic ionic liquids ([Emim][Oac]) of *Song et al.(2014)* [57] as catalyst at the conditions described by *McKeown et al.(2020)* [38]. These described conditions were: a mass ratio of 12:2:1 (water/PLA/IL), 130 °C and 2 hours reaction time. However, the hydrolysis did not give good results. This did not give the described conversion of 90.86%. Afterwards, the amount of PLA was reduced and the PLA was milled to a smaller size (5mm – 0.5 mm), and the reaction time was increased. This gave better results, but also caused the ionic liquid to decompose, which interfered with the measurement. After applying the correction associated with the decomposition, the conversion turned out to be 95.56% at a mass ratio of 6:1:0.5 (water/PLA/IL), 130 °C and 5.5 hours reaction time.

Next, the hydrolysis was repeated with these latter conditions, but with the synthesized 2-hydroxyethyl ammonium acetate as catalyst. This reaction gave a conversion of 97.71%, which is better than the best result reported in *Song et al.(2014)* [57] for the aprotic ionic liquid [Bmim][Oac] (93.93%). However, it has to be noted that the [Bmim][Oac] was only given a reaction time of 2 hours, which means that the conversion might be similar or even better than the one obtained for 2-hydroxyethyl ammonium acetate if it was given the same reaction time.

The conversions of the hydrolysis with 2-hydroxyethyl ammonium acetate was slightly better than the one obtained for the hydrolysis with [Emim][OAc]. Due to the greener character of the protic ionic liquids and the lower production cost, it is advised to use the protic ionic liquid.

Unfortunately, due to the Corona outbreak it was not possible to synthesize the bis-(2-hyrdoxyethyl ammonium) acetate and the tris-(2-hyrdoxyethyl ammonium) acetate protic ionic liquids and to properly characterize the L-menthol-decanoic acid deep eutectic solvent with FT-IR and H-NMR. The measurements the thermophysical properties of the above-mentioned solvents, together with the performance of the above-mentioned protic ionic liquids produced in this work in the hydrolysis of poly (lactic acid) could also not be performed for the same reason. With other words, further research into these solvents and the showcasing of their applications such as the hydrolysis of poly (lactic acid), the pretreatment of biomass and the extraction of aqueous alcohol mixtures is necessary.

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Appendix A: Sustainability reflection

Sustainable development has been defined in many ways, but the most used definition is the one described in *Our common future*, also known as the Brundtland report: *“ Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs”*. It is this sustainable development that is the foundation for today’s leading global framework for international cooperation – the 2030 agenda for sustainable development. This agenda mentions 17 sustainable development goals (SDGs) (Figure 70) with each a specific target that needs to be achieved by 2030. These goals are universal and require actions on all fronts of society. In this context, this section is devoted to the discussion of the relationship between some of the 17 SDGs and the solvents discussed in this work and their applications.

Figure 70: The 17 sustainable development goals [67]

The first SDG that will be discussed is number three: good health and well-being. As the name indicates, this goal as all about the health and well-being of living organisms and the environment. Like mentioned in the introduction, the main problem with the use of traditional VOCs in industrial applications like media for different types of reactions, extraction fluid, etc. is that they are volatile and toxic, which makes them a threat for the health and well-being of both living organisms and the environment. The primary purpose of the ionic liquids and the deep eutectic solvents id to replace the VOCs as non-volatile alternatives. The DES are slightly better alternatives than the ionic liquids since they have a a lower or non-existent toxicity and e a significantly high biodegradability.

Besides the solvents themselves, there is also the application of DES in the liquid-liquid extraction of aqueous alcohol mixtures that can be placed underneath this SDG. In this application, the DES do not only extract alcohols that could be harmful for living organisms. With other words, the DES reduces the amount of harmful chemicals from both classes in the wastewater stream and thus also reduces the amount of these chemicals released in the environment. The DES, ILs and this application can also be linked to SDG 9: Industry, innovation and infrastructure, since they promote the use of clean and environmentally friendly technologies and industrial processes.

Another SDG that can be related to this work is SDG 12: Responsible production and consumption. This SDG is about everything that has to do with reducing the amount of waste and the efficient usage of natural resources. This can be directly related to the application of the PILs in the pretreatment of biomass and their application in the hydrolysis of PLA. Lignocellulosic biomass leftover from oil-extraction processes or from the paper-industry is usually thrown away or incinerated for energy, because this biomass is difficult to process. The use of PILs in the pretreatment of this biomass can make it more accessible for chemical and/or enzymatic processes. This would allow the production of valuable chemicals, that are now usually produced from fossil fuel resources, from this leftover biomass.

PLA is a plastic that is considered biodegradable, but its degradation can still take years depending on the conditions. The current methods of mechanical recycling elongated the lifetime of the PLA, but after each mechanical recycling, the quality of the PLA decreases. This limits the application of this PLA to applications which do not require PLA of a high quality. After a few times, the PLA cannot be reused anymore and has to be wasted. However, chemical recycling methods, like hydrolysis, allows the polymer to decompose into its building block (lactic acid). This lactic acid can then be used again to produce PLA with the same quality. With other words, chemical recycling can minimize or even eliminate the amount of PLA waste. The use of PILs as catalysts in the hydrolysis and reducing the hydrolysis temperature or increasing the yield, makes the chemical recycling even more environmentally friendly.

The latter application can also be related to SDG 14: life under water, since the reduction in the amount of PLA waste also means a reduction of the PLA amount that ends up in the sea where it can pose a danger for living organisms. Future research might even prove that PILs can be used in the chemical recycling of other plastics.

Even though the relationship between the solvents and their applications and SDG 3, 9, 12 and 14 is clear, the relationship between these and the other 13 SDGs is less obvious or even non-existent. However, more research into PILs, DESs and their applications might create new connections between them and the remaining 13 SDGs.