Design and applications of hydrophobic deep eutectic solvents

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Design and Applications of Hydrophobic Deep Eutectic Solvents

Dannie van Osch

Design and Applications of Hydrophobic Deep Eutectic Solvents

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit
Eindhoven, op gezag van de rector magnificus prof.dr.ir. F.P.T. Baaijens,
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door

Dannie Jozef Gerardus Petrus van Osch

geboren te Geleen

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The cover of this thesis was designed by Bart Zijlstra following the idea of Marjorie du Pree and Dannie van Osch. The front cover shows the formation of droplets of deep eutectic solvent (DES) from two solid starting components, while the back cover shows that one droplet of DES falls in a water phase and emulsifies.

Contents

Chapter 1

Introduction to Innovative Solvents

1.1 Why do we need innovative solvents?

It is generally accepted that the use of organic solvents is of great environmental concern.[1] Specifically if they are particularly hazardous and increase the carbon footprint, while a reduction in carbon footprint is needed, as acknowledged by the European Union. For 2020 the EU introduced rules on 'climate and energy package',[2] which states that their should be a 20% cut in greenhouse gas emissions, 20% of energy via renewables and 20% improvement in energy efficiency. Before 2050 the EU desires a 'low-carbon economy' via a cut in greenhouse gas emissions of 80%.[3]

Leading starting points to reduce environmental hazards are the twelve principles of Green Chemistry, which were established by Anastas and Warner in their book 'Green chemistry: theory and practice'.[4] These principles are:

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Less Hazardous Chemical Syntheses**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals**
   Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. **Safer Solvents and Auxiliaries**
   The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. **Design for Energy Efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real-time Analysis for Pollution Prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

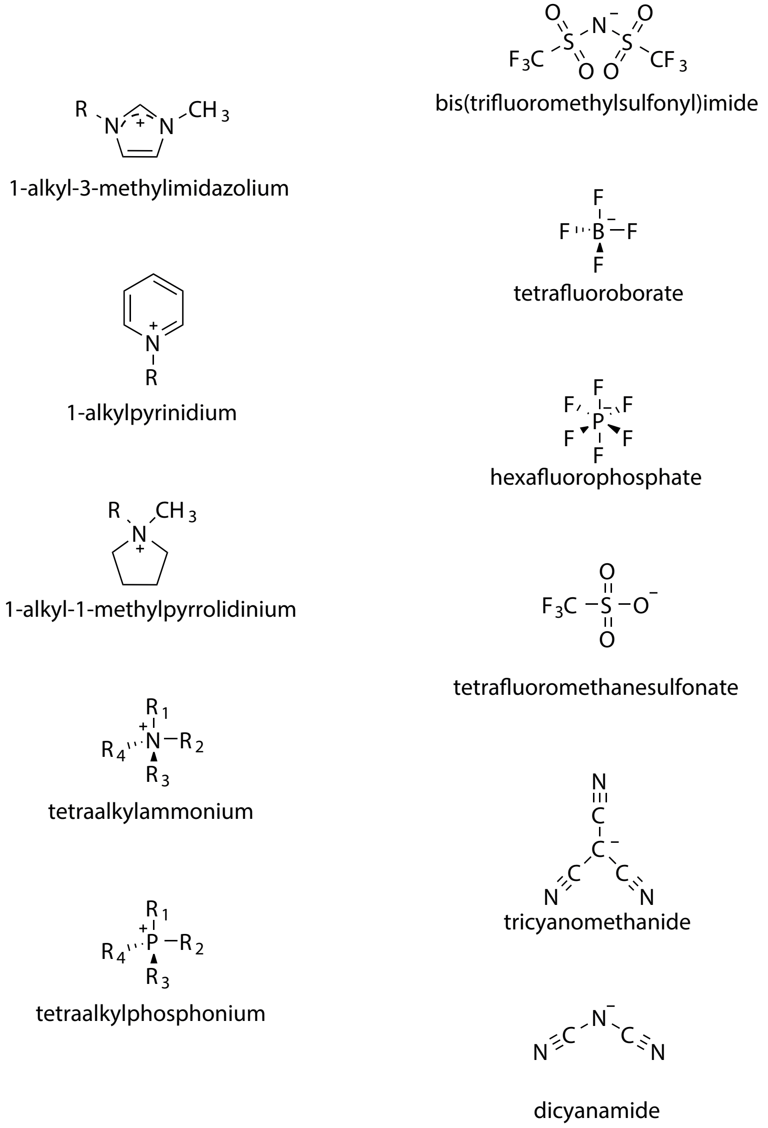
These can be summarized as "the design, development, and implementation of chemical products and processes that reduce or eliminate the use and generation of substances hazardous to human health and environment."[4] As mentioned before, one of the main hazardous constituents of chemical processes are solvents. Thus, from the viewpoint of Green Chemistry more environmentally friendly solvents, termed designer or innovative solvents, should be developed to replace the ones currently used in industrial processes.

Active research has been performed in recent years into replacing solvents. Two categories of innovative, designer solvents have been investigated. These are ionic liquids (ILs) and deep eutectic solvents (DESs).

1.2 Ionic liquids and deep eutectic solvents: definition and preparation methods

Ionic liquids are considered as the first generation of innovative solvents. ILs are salts composed of an organic cation and an organic/inorganic anion with a melting temperature below 373 K. They may even be often liquid at room temperature.[5] ILs are regarded as designer solvents due to the large number of possible combinations of cations and anions to prepare ILs, which leads to a wide tunability of their physicochemical and toxicological properties.[5] Compared to conventional organic solvents, unique properties such as the low volatility of ILs favors their use in a variety of applications, for example in synthesis and catalysis, electronic devices, thermal fluids and separations.[6–10]

The field of ILs can be subdivided into two classes, i.e. aprotic ionic liquids (AILs) and protic ionic liquids (PILs). Depending on the type of IL, the synthesis is conducted by different procedures, which have been reviewed in the literature. Several detailed synthesis methods have been devised,[5,9,11–15] but the most common synthesis of AILs is the quaternization of an amine, phosphine or sulfide with haloalkanes upon the formation of a halide salt. The second step is the anion metathesis reaction by addition of a metal salt, whereby the halide anion is exchanged for the salt anion. In Figure 1.1 the most widely used cations and anions of AILs are shown.



1-alkyl-3-methylimidazolium

1-alkylpyrinidium

1-alkyl-1-methylpyrrolidinium

tetraalkylammonium

tetraalkylphosphonium

bis(trifluoromethylsulfonyl)imide

tetrafluoroborate

hexafluorophosphate

tetrafluoromethanesulfonate

tricyanomethanide

dicyanamide

Figure 1.1: Commonly used cations and anions for aprotic ionic liquids.

PILs are easily prepared by proton transfer from a Brønsted acid to a Brønsted base, in equimolar proportions.[13] The preparation of a PIL is most commonly an exothermic reaction, so cooling is necessary. For PILs it has to be considered that there is a possibility that they are not only composed of ions, but may also contain neutral molecules ($<$1%) due to the dependence on the acid–base equilibrium.[13] In Figure 1.2 some representative cations and anions for PILs are presented.

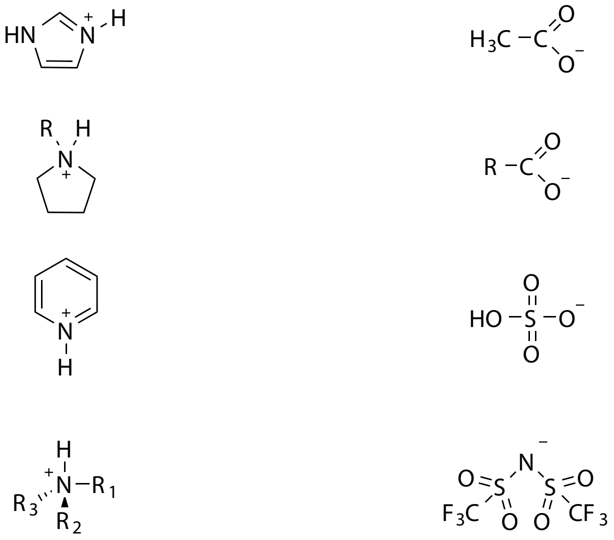


Figure 1.2: Commonly used cations and anions for protic ionic liquids.

Major disadvantages of ILs are their toxicity, complicated synthesis and need for purification. This makes them expensive and not preferable for the chemical industry, so there was a clear need for other innovative solvents. Preferably, such solvents should have similar physicochemical properties as ILs, but can be easily prepared from readily available compounds. This explains the interest leading to the development and focus on deep eutectic solvents (DESs).

DESs are a combination of two solid components that undergo entropy of mixing, hydrogen bonding and Van der Waals interactions, lowering the melting point of this complex. It is generally stated that one component behaves as a hydrogen bond donor (HBD) and one as a hydrogen bond acceptor (HBA). DESs are generally easy to prepare. In the most easy and commonly used preparation method, the heating method, the two solid constituents of the DES are mixed together and heated until a liquid is formed. No additional solvent is needed and no reaction occurs. Consequently, no purification steps are needed, making them promising and economically viable alternatives for conventional organic solvents and ILs.[16–18]

Other methods reported for the preparation of DESs are the vacuum evaporating, grinding and freeze-drying methods. In the evaporating method, the components are dissolved in water, after which the majority of water is evaporated at 323 K under vacuum. The final mixture is kept inside a desiccator with silica gel until it reaches a constant weight.[19] In the grinding method the two solid components are added to a mortar, after which they are grinded until a clear, homogeneous liquid is formed, typically under a nitrogen atmosphere and inside a glovebox.[20] In the freeze-drying method, both the HBD and the HBA are dissolved in approximately 5 wt% of water. These two solutions are mixed, frozen and subsequently freeze-dried to form a clear, homogeneous liquid.[21] Figure 1.3 illustrates some of the HBDs and HBAs that have been used to prepare DESs.

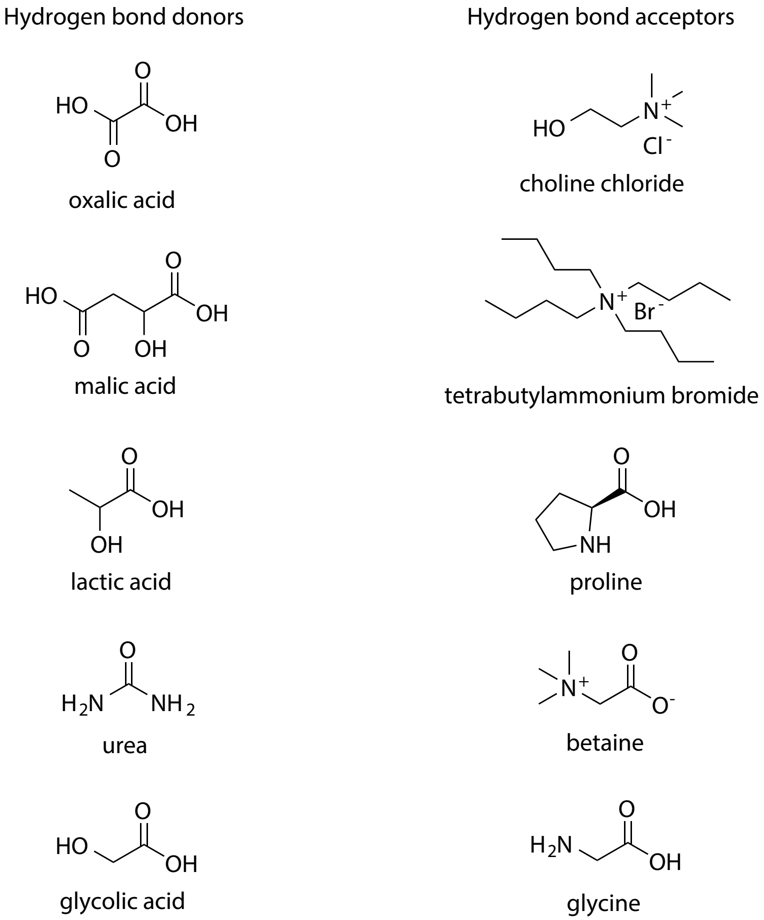


Figure 1.3: Structures of some hydrogen bond donors and hydrogen bond acceptors used to form deep eutectic solvents.

1.3 Physicochemical properties of deep eutectic solvents as compared to ionic liquids

Since it is often noted that DESs are the next generation of designer solvents, the successors of the ILs, here some physicochemical properties of both designers solvents are presented.

1.3.1 Density

The density of a material depends on how lightly the molecules can pack together, which in turn is related to the size mass and shape of their molecules and intermolecular interactions. The densities of most of the ILs range between 800 and 1600 $\mathrm{kg \cdot m^{-3}}$.[22–25] Literature reviews of thermophysical properties have been published, describing the main aspects of the effect of the cation or anion, impurities and methodologies.[5,23–30]

DESs have densities within the same range as ILs. Following the trend that was observed for ILs, the densities of DESs decrease with an increase of the alkyl chain lengths of their components.[20,31–36] It was also observed that the densities decrease as the relative ratio of a salt as HBA to HBD is increased.[37,38]

1.3.2 Viscosity

The shear viscosity is an important property, which describes the internal resistance of a fluid to shear stress. At ambient temperature, ILs have a higher viscosity (around 10 $\mathrm{mPa \cdot s}$ to 10^3 $\mathrm{mPa \cdot s}$) than typical molecular liquids (around 0.2 $\mathrm{mPa \cdot s}$ to 10 $\mathrm{mPa \cdot s}$).[5,23,39] The viscosity of an IL depends on the combination of the cation and anion and on impurities present, effects that are well studied in the literature.[5,23,40–42] For example, the presence of very low concentrations of chloride drastically increases the viscosity, whereas the presence of water significantly reduces it.[43–48]

DESs exhibit relatively high viscosities. Depending on the combination of the HBD and HBA viscosities above 10^4 $\mathrm{mPa \cdot s}$ can even be reached.[49] The viscosity of a DES is mainly affected by the chemical nature and ratio of its components, the temperature and the water content. Recently, the addition of water has been presented as a method to tailor the viscosity of DESs.[21,50,51] However, it should be noted that individual DES components can be fully solvated at water contents between 25 and 50 wt%.[50,51] Hence, if the specific DES properties are to be preserved, there are limits to the addition of water to tailor the viscosity. In general, in a IL or a DES, the decrease of viscosity with increasing temperature is more pronounced than in a molecular liquid.[20,23,26,31,32,35,52,53] The higher viscosities are directly related to their intermolecular interactions. The increase of the temperature will considerably decrease their intensity and consequently decrease the viscosity.

1.3.3 Thermal phase behavior

Both AILs and PILs exhibit a wide liquid range, which depends on the lower temperature limit (glass formation or crystallization) and the upper temperature limit (usually the thermal decomposition temperature) of the liquid window. For many ILs, the cooling of the liquid phase goes through a metastable state (supercooling), and later to a glass transition, which is detected typically in the region between 173 and 213 K. In some cases multiple solid–solid transitions have been observed.[54–56]

DESs are usually composed of asymmetric components contributing to a decrease of the lattice energy and consequently attain lower melting temperatures than the pure components.[57] The melting temperature of DESs is related to the interactions between the HBD and HBA. DESs are characterized by having a lower melting temperature than the individual components. DESs that are liquid at room temperature are the focus of current increasing research activities in the field.[31,57–59]

Like ILs, some room temperature DESs do not crystallize readily, but undergo a supercooled state or glass transition.[19,20,32] In other cases, their thermal behavior is quite complex and they can exhibit multiple solid–solid transitions or plastic crystal behavior.[60] The glass transition of DESs is typically detected in the region between 173 and 213 K, as observed for ILs.[17,20,31,32,57,58,61] Regarding the thermal stability, most of the reported DESs present a decomposition temperature near 473 K or below, being relatively less stable than ILs.[19,31,32,57,58]

1.3.4 Toxicity

ILs and DESs are usually regarded as 'green' solvents, especially due to their low volatility. However, the high solubility in aqueous media represents a risk to the aquatic environment. The stability of ILs makes them poorly decomposable by microorganisms,[62–65] persisting in the environment for some time.[66] The antimicrobial activity towards microorganisms in a wide range of ILs was investigated.[67,68] Most importantly, an increase of toxicity with the increase of the cation alkyl chain length was observed. One of the main advantages of DESs is the promising low toxicity compared to ILs. DESs have usually been considered as non-toxic solvents, due to the use of natural and safe components that are readily available. The toxicity of phosphonium based DESs was evaluated and it was found that the toxicity depends on the composition, viscosity and molar ratio of the two components.[69] Additionally, the toxicity of the DESs was compared with that of the individual constituents, and it was found that the studied DESs presented either higher or lower toxicity.[69] Thus, most likely it will all depend on the components that are used for the DESs and the effects that the mixing of the two components has on their toxicity. More information on toxicity of DESs can be found in the literature.[59,66,70]

1.4 Can DESs be considered as ’green’ solvents?

A main question that has to be answered for DESs is whether they can be considered as ’green’ solvents. In general, it is accepted that DESs are denoted as the next generation of solvents, overcoming disadvantages of ILs.[58] The biggest disadvantage of ILs is the fact that they are expensive due to their preparation by a chemical reaction of the components followed by extensive purification.

However, as also mentioned in section 1.3.4 only a few papers discussed the toxicity of the DESs so far. Moreover, the topic of performing measurements on the biodegradability of DESs is hardly touched in the literature. These two aspects will become key for the future of the field of DESs. Even if DESs can be used for the most elegant applications, it is their toxicity and biodegradability that will determine whether they can truly be a worthy replacement for the solvents currently used in the industry.

Most likely a first estimation for the toxicity and biodegradability of a DES can be made from the pure components. As demonstrated for DESs prepared from natural components,[71,72] often denoted as natural deep eutectic solvents (NADES), it are these components that make a DES a more sustainable solvent in comparison to conventional ones. Even when ignoring synergistic effects, it is a strong asset that 'green' DESs can be produced from natural components, provided that these natural components are biodegradable and low toxic.

1.5 Applications of hydrophilic deep eutectic solvents

The field of DESs is expanding rapidly, which is also shown from the amount of DESs reported in the literature. In total 1860 publications have been presented in the field of DESs, of which 544 were presented in 2017 (Scopus May 2018). New applications of DESs arise nearly every day. Here, a short overview will be given of some applications that have been extensively investigated with DESs. For broader overviews in the field of DESs the reader is directed to the available literature.[31,57,58]

Arguably, the most investigated application so far, is the use of DESs for the processing of metals, the field where DESs were first applied. It was shown that DESs can be used for metal electrodeposition of metals such as chrome, aluminium, copper, nickel and zinc. Moreover, the deposition of alloy coatings and composite coatings were also investigated.[57]

Another field in which DESs have shown their potential is synthesis. Examples include polymerizations, base- and acid-catalyzed reactions, transition metal-catalyzed reactions and bio-catalysis.[31]

It has also been suggested that lignin derivatives can dissolve in DESs, which opens the field of biomass processing with them.[17] Recently, a few papers claimed that lignin can be extracted with DESs.[73]

A field that is not yet much explored much is liquid-liquid extractions, especially not from water. Arguably, this is due to the fact that extractions from the water phase are not possible since there were no hydrophobic DESs reported, so far.

1.6 Outline of the thesis

The main focus of this thesis is on the design and applications of *hydrophobic* DESs. This thesis is organized in such a way that after the introduction it systematically informs the reader more about hydrophobic DESs. Starting with the discovery of DESs, it follows with the search of more sustainable ones and applications that can be performed with them.

Chapter 2 introduces hydrophobic DESs and their physicochemical properties including the cross-contamination of the DES and water phase in liquid-liquid extractions. The removal of volatile fatty acids from water is investigated as potential application.

Chapter 3 describes a systematic search into more sustainable hydrophobic DESs, based on terpenes. Many combinations were tested to obtain more hydrophobic DESs. After this initial screening four criteria are set to test their sustainability after use for extraction.

Chapter 4 is about the capture of carbon dioxide (CO_2) with hydrophobic DESs. Decanoic acid based hydrophobic DESs as presented in Chapter 2 were used for this application. The influence of different parameters such as the molar volume, the type of anions and the temperature on CO_2 solubility are studied. The results of the hydrophobic DESs are compared with ILs. A predictive model based on Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) is used to predict solubilities of CO_2 in hydrophobic DESs and is compared to the experiments.

In Chapter 5 hydrophobic DESs are tested for metal ion extraction from water. Transition and alkali metal ions are studied. Further, different concentrations of Co^{2+} in the water and different mass ratios of DES-to-water are investigated. It is also tested within how much time Co^{2+} is removed from the water phase. Finally, the extraction mechanism is evaluated.

Chapter 6 reveals how hydrophobic DESs can be used for the preparation of oil-in-water emulsions. Light scattering is used for measuring the evolution of the droplets over time. Different parameters such as the concentration of the surfactant and the mass fractions of the DES were studied to check their influence on the droplet growth. Moreover, the addition of salt on the droplet evolution is tested.

Finally, a summary of the main results obtained in this thesis and an outlook is presented in Chapter 7.

Chapter 2

The Introduction of Hydrophobic Deep Eutectic Solvents

Abstract

Hydrophobic deep eutectic solvents (DESs) are presented. They consist of decanoic acid and various quaternary ammonium salts. The effect of the length of the alkyl chains on the hydrophobicity and the equilibrium of the two-phase DES-water system were investigated. It is shown that these DESs can be used for the recovery of volatile fatty acids from diluted aqueous solutions.

This chapter is a modified version of:
Dannie J.G.P. van Osch[1], Lawien F. Zubeir[1], Adriaan van den Bruinhorst, Marisa A.A. Rocha, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents as Water-immiscible Extractants, *Green Chem.*, 2015, **17**, 4518-4521
[1]**combined first authorship**

2.1 Introduction

The field of deep eutectic solvents (DESs) was developed around 2002 and since then the focus has been on hydrophilic DESs.[16,31,58] These DESs are not applicable in a water rich environment, for certain applications such as extractions, since they would dissolve in the aqueous environment. A hydrophobic variant widens the field of applications to include water-immiscible solvents. Many processes have the possibility to become more effective by using these hydrophobic solvents, due to their advantages over ionic liquids (ILs) and conventional solvents. Moreover, an ionic character of the hydrogen bond acceptor (HBA) of these hydrophobic DESs could offer an advantage in many liquid–liquid extraction processes, as was shown before for ILs.[10,74–76]

This chapter discusses the first hydrophobic DESs presented as such in the literature. It is however debatable if earlier reports of hydrophobic DESs have been presented in the literature. In Chapter 5 we use combinations of decanoic acid and lidocaine for the removal of metal ions from non-buffered water.[77,78] A combination of solids that is mentioned in the literature as a deep eutectic mixture, not stating if it is hydrophilic or hydrophobic.[77,78] While in this thesis different hydrophobic DESs and applications will be discussed, we would like to supply the reader with some additional information regarding hydrophobic DESs as presented in the literature. A few months after the work of this chapter was presented, menthol based hydrophobic DES were presented in the literature, which were used for the removal of caffeine, tryptophan, vanillin and isophthalic acid from water.[79]

In the meanwhile, hydrophobic DESs have shown their value in the scientific literature for a range of applications. These include metal ion removal from pH adjusted water,[80] and the removal of furfural and hydroxymethylfurfural with a hydrophobic DES membrane.[81] Moreover, hydrophobic DESs were used for performing microextractions,[82,83] and for the task-specific extraction of components from leaves.[84,85]

In this chapter hydrophobic DESs are presented that consist of a fatty acid and a quaternary ammonium salt. Decanoic acid (DecA) was chosen as hydrogen bond donor (HBD) for its high hydrophobic behavior in combination with its limited ability to undergo hydrogen bonding interactions. The solubility of DecA in water is only $0.15\,\mathrm{mg \cdot g^{-1}}$ at 293 K.[86] As HBAs, 6 quaternary ammonium salts were chosen, namely tetrabutylammonium chloride ($N_{4444}-Cl$), methyltrioctylammonium chloride ($N_{8881}-Cl$), tetraheptylammonium chloride ($N_{4444}-Cl$), tetraoctylammonium chloride ($N_{8888}-Cl$), methyltrioctylammonium bromide ($N_{8881}-Br$) and tetraoctylammonium bromide ($N_{8888}-Br$). Their physicochemical properties will be discussed, followed by the cross-contamination of the DES and water phase, which depends on the length of the carbon chains of the quaternary ammonium salts. Finally, the studied DESs will be evaluated as extractants for volatile fatty acids (VFAs) from dilute aqueous solutions. The obtained extraction efficiencies at room temperature (295 K) will be compared with trioctylamine (TOA) as extracting agent.

2.2 Experimental section

2.2.1 Materials, preparation and extraction method

Materials for the preparation

Tetrabutylammonium chloride ($N_{4444}-Cl$) was purchased from Merck with a purity ≥95%, tetraheptylammonium chloride ($N_{7777}-Cl$) was obtained from Acros Organics with a 95% purity and methyltrioctylammonium chloride ($N_{8881}-Cl$), tetraoctylammonium chloride ($N_{8888}-Cl$), methyltrioctylammonium bromide ($N_{8881}-Br$) and tetraoctylammonium bromide ($N_{8888}-Br$) were acquired from Sigma-Aldrich with purities of 97%, 97%, 97% and 98%, respectively. Decanoic acid was purchased from Sigma-Aldrich with a purity higher than 98%. The chemical structures are presented in Figure 2.1.

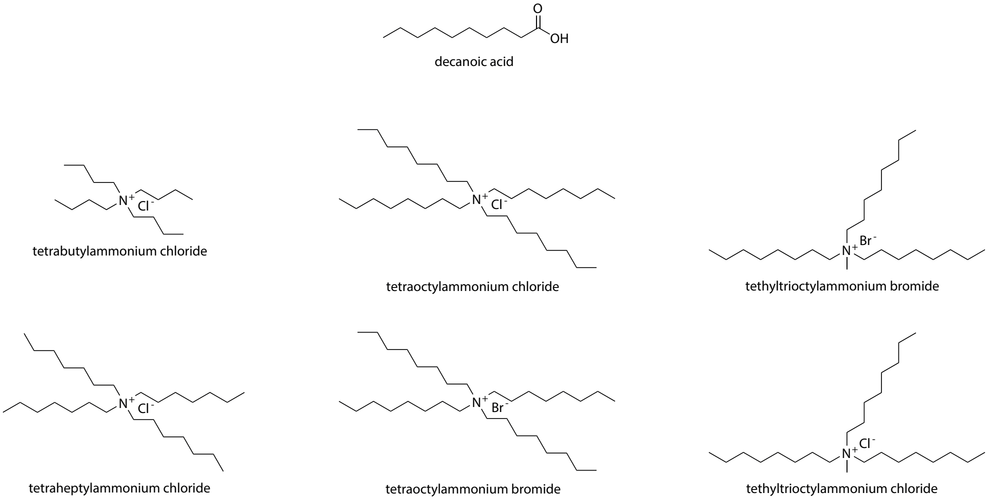


Figure 2.1: Chemical structures of the components used for the preparation of the hydrophobic DESs.

Materials for the mixing with water and the extraction

The volatile fatty acids (VFAs) propionic acid (≥99.5%) and butyric acid (≥99%) were acquired from Sigma-Aldrich. Acetic acid (glacial, 100%) was obtained from Merck. These chemicals were used as provided. MilliQ water was used for the preparation of the solutions and for the mixing of the DESs with water, which was obtained from a Millipore Milli-Q® biocel, which used a Q-grade® column.

Preparation

The six deep eutectic solvents (DESs) were all prepared following the same experimental method. The hydrogen bond donor (HBD), decanoic acid, was first weighted in a flask. The hydrogen bond acceptors (HBAs), the quaternary ammonium salts, were first weighted in a weighing boat. The amount of HBA was mixed with the amount of HBD in the flask. The flask was then heated in an oil bath at a temperature of 323 K until it was a clear liquid. The wall of the flask was rinsed with the DES inside the flask to ensure that all the solid was in the liquid phase. After rinsing the flask was again heated up to 323 K until again a clear liquid was obtained. Afterwards, the DES was maintained at room temperature (295 ± 1 K) overnight.

Mixing with water

All the DESs were mixed with water to investigate the amount of water they would uptake. Centrifuge tubes (CELLSTAR®) of 50 mL were used, in which 6 grams of water and 6 grams of DES was added. The mixture was vigorously stirred with a vortex mixer for 1 minute (VWR, analog Vortex Mixer) and afterwards placed in the centrifuge (Sigma 2-16 KL) for 30 min at 12000 rpm. The phases were separated and further analyzed. From the top phase (DES-rich phase) the water content was determined using Karl Fischer titration and the bottom phase (water-rich phase) was analyzed with ion chromatography (IC).

Liquid-liquid extraction method

Liquid-liquid extractions were conducted using the prepared hydrophobic DESs as extractants at room temperature (295 ± 1 K). Solutions of 1 wt% VFA in water were prepared, with a final pH of 3.3. In centrifuge tubes, 2 mL aliquots of VFA solutions were mixed with 2 mL of hydrophobic DES. The mixtures were initially mixed for 10 s using a vortex mixer and later for 2 hours, at room temperature, using an incubating shaker (IKA KS 4000 I). The samples were centrifuged (Sigma 2-16 KL) for 30 min at 3500 rpm. Thereafter, the DES-rich phase and water-rich phase were taken using a needled syringe. The concentration of the VFAs in the aqueous phase was determined by analysis of 1 mL samples using high performance liquid chromatography (HPLC). The same experimental methodology was used for the extraction experiments using trioctylamine.

2.2.2 Analytical methodologies

Water content determination

The water content in the prepared DESs was measured with the Karl Fischer titration method (795 KFT Titrino Metrohm Karl Fischer).

Density and viscosity

Density, ρ, and dynamic shear viscosity, η, were measured with an Anton Paar SVM 3000 Stabinger Viscometer. The measurements were performed in the temperature range of (288.15 - 323.15) K at atmospheric pressure. The temperature uncertainty in the temperature range of the equipment (288.15 to 378.15 K) is $\pm$ 0.02 K and the relative uncertainty of the dynamic viscosity is $\pm$ 0.35 %, while the absolute uncertainty in the density is $0.5\,\mathrm{kg}\cdot\mathrm{m}^{-3}$.

Thermal gravimetric analysis (TGA)

The decomposition temperatures of all the studied hydrophobic DESs were determined using a thermogravimetric analyzer (Perkin Elmer TGA 4000). The samples were heated in a ceramic crucible under a continuous nitrogen flow ($20\,\mathrm{mL}\cdot\mathrm{min}^{-1}$) and a gas pressure of 0.2 MPa. The thermal stability was determined by scanning in the temperature range of (303 - 673) K at a heating rate of $5\,\mathrm{K}\cdot\mathrm{min}^{-1}$. The sample masses were typically between 15 and 30 mg and the weighing precision and sensitivity of the balance are $\pm$ 0.01% and 1 µg, respectively. The spectra are presented in paragraph 2.5.1.

Nuclear magnetic resonance (NMR)

Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectra were recorded on a 400 MHz Bruker BZH 400/52. All samples were diluted with deuterated dimethyl sulfoxide (DMSO-d_6) without further pretreatment inside 8″ Wilmad precision tubes with an outer diameter of 5 mm. A relaxation time of 3 s was applied and the spectra were recorded in 16 scans. The signals were automatically Fourier transformed with recording software VnmrJ. Further adjustments were performed with software package MestreNova, version 9.1.0-14011. Phase corrections and integrals were done manually, while baselines were corrected with the Bernstein polynomial (6 parameters). The spectra are presented in paragraph 2.5.2.

Differential scanning calorimetry (DSC)

The melting point and solid-solid transition temperatures of the prepared DESs were studied using differential scanning calorimetry (TA instruments, DSC Q100). The measurements were conducted within a temperature range of 193 to 323 K at a heating rate of $5\,\mathrm{K} \cdot \mathrm{min}^{-1}$. The temperature measurement is accurate within ± 0.1 K. The calorimeter precision and sensitivity are ± 0.1 % and 0.2 µW, respectively.

Fourier-transform infrared (FTIR) spectroscopy

All Fourier transformed infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum Two spectrometer equipped with a Spectrum Two UATR (universal attenuated total reflectance) module. All samples were scanned over a wavenumber range of 450 - 4000 cm^{-1}. The spectra of the DESs were recorded in 16 scans, for the pure components 4 scans were sufficient. Prior to each measurement, the quality of the background signal was evaluated and a background spectrum was recorded using the same settings as for the sample measurement if necessary (residual peaks after cleaning >0.2 % transmittance). For liquids, the crystal of the UATR module was completely covered with a small drop of the sample. Solids were pressed on the crystal until a maximum signal of at least 50 % transmittance was obtained. The spectra were submitted to an automatic baseline correction performed with the PerkinElmer Spectrum software, Application version 10.03.08.0135, 2012. The spectra are presented in Appendix 2.5.3.

High-performance liquid chromatography (HPLC)

The aqueous phases after extraction were analyzed using an Agilent Technologies 1260 Infinity HPLC system, with a 300 mm x 7.8 mm Aminex HPX-87H column, using a UV detector operating at a wavelength of 210 nm. The injection volume was 10 µL, the temperature of the column was kept at 323 K and 5 mM aqueous sulphuric acid was used as eluent with a flow rate of $0.6\,\mathrm{mL}\cdot\mathrm{min}^{-1}$. Based on the concentrations in the water, the distribution coefficients (K), were calculated from the VFA concentration in the water-rich phase before, $C^{\mathrm{aq}}_{\mathrm{VFA,0}}$, and after the extraction, $C^{\mathrm{aq}}_{\mathrm{VFA,1}}$:

$$K = \frac{C^{\mathrm{aq}}_{\mathrm{VFA,0}} - C^{\mathrm{aq}}_{\mathrm{VFA,1}}}{C^{\mathrm{aq}}_{\mathrm{VFA,0}}} \tag{2.1}$$

Ion chromatography (IC)

The chloride and bromide concentrations were measured with a Metrohm 761 Compact IC and 762 IC interface with a detection limit of $0.1\,\mathrm{mg}\cdot\mathrm{L}^{-1}$.

2.3 Results and discussion

2.3.1 The production of hydrophobic DESs

For the production of hydrophobic DESs it was chosen to use decanoic acid, a long fatty chain acid, and six quaternary ammonium salts. These six quaternary ammonium salts are: tetrabutylammonium chloride ($N_{4444}-Cl$), tetraheptylammonium chloride ($N_{7777}-Cl$), methyltrioctylammonium chloride ($N_{8881}-Cl$), tetraoctylammonium chloride ($N_{8888}-Cl$), methyltrioctylammonium bromide ($N_{8881}-Br$) and tetraoctylammonium bromide ($N_{8888}-Br$). Their chemical structures are presented in Figure 2.1.

All hydrophobic DESs were prepared in a 2:1 molar ratio of the decanoic acid:quaternary ammonium salt. Thus, six hydrophobic DESs were prepared. To investigate their hydrophobicity, they were mixed with water in a 1:1 mass ratio. An example of one of the hydrophobic DESs upon mixing with water is shown in Figure 2.2.

Figure 2.2: DecA:$N_{8888}-Br$ (2:1) after mixing with water. A 1:1 mass ratio of DES and water was used.

2.3.2 Physicochemical properties of the hydrophobic DESs

In Table 2.1 some physicochemical properties (densities, dynamic viscosities, decomposition temperatures, melting points and water contents) of the newly prepared hydrophobic DESs are presented, while Figures 2.3 and 2.4 show the densities and viscosities as a function of temperature.

Table 2.1: Physicochemical properties of the prepared deep eutectic solvents (DESs). Density (ρ) and viscosity (η) data are measured at 298.15 K. The water contents correspond to the DES after preparation.

DES	$w_{\mathrm{before,H_2O}}$ [wt %]	ρ [$\mathrm{kg \cdot m^{-3}}$]	η [$\mathrm{mPa \cdot s}$]	T_m [K]	T_d [K]
DecA:$N_{4444}-Cl$ (2:1)	0.81	916.8	265.26	261.2	467.79
DecA:$N_{8881}-Br$ (2:1)	0.32	942.2	576.53	282.1	459.31
DecA:$N_{8881}-Cl$ (2:1)	0.26	896.4	783.41	273.1	472.41
DecA:$N_{7777}-Cl$ (2:1)	0.77	890.7	172.87	256.5	472.37
DecA:$N_{8888}-Br$ (2:1)	0.09	929.8	636.86	282.1	465.24
DecA:$N_{8888}-Cl$ (2:1)	0.46	888.9	472.58	275.1	480.81

The onset decomposition temperatures (Table 2.1 and paragraph 2.5.1) as measured by TGA are rather high, which allows the use of the DESs at elevated temperatures. In combination with the low melting points, this results in a wide range where the DES is a liquid. In contrast to an earlier reported DecA based DES,[78] no deprotonation of the acid could be observed for any of the solvents presented here. From FTIR analysis, it can be seen that the stretch vibration of C=O stretch corresponds to a single sharp peak for pure DecA, which is broadened due to hydrogen bonding, but maintained for all quaternary ammonium salt based DESs (see the figures in paragraph 2.5.3). This could be justified by the fact that the ammonium cation is unable to accept a proton from the decanoic acid.

The densities at 298.15 K are within the range of 889 to 942 $\mathrm{kg \cdot m^{-3}}$, which is considerably lower than found for most hydrophilic DESs and water.[58] The low densities of these DESs can be explained by the low densities of both constituents used to prepare the DESs. The viscosities are moderate, varying between 173 and 783 mPa · s at 298.15 K.

It is hypothesized that the large differences between the viscosities can be associated with the strength of interaction between the HBD and the HBA. Furthermore, the following trends are observed: (i) the longer the alkyl chain length, the higher the viscosity, and (ii) salts containing a bromide anion have higher viscosities compared to those containing a chloride anion. This is in agreement with the trend observed in ILs.[23,87]

The densities and viscosities were also investigated over a temperature range of 288.15 K to 323.15 K as shown in Figure 2.3 and 2.4.

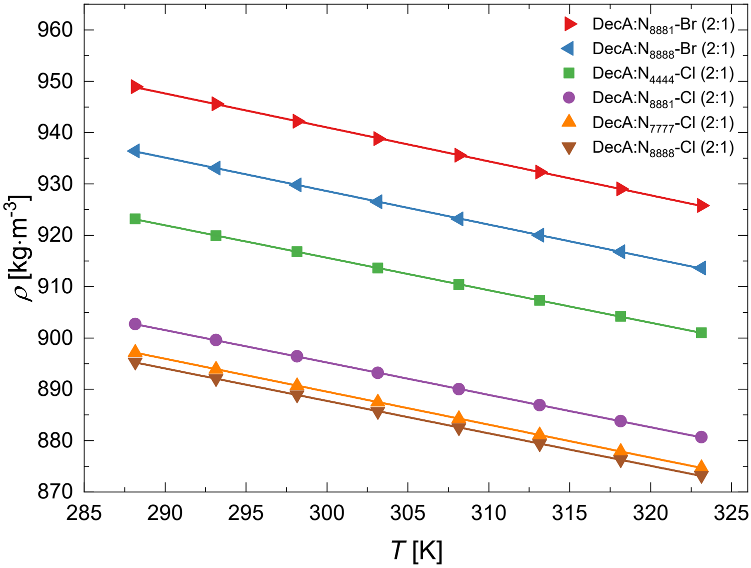


Figure 2.3: Densities over temperature. The lines are added for clarification purposes.

The variation in densities can be described with the following linear correlation.[88,89]

$$\rho = a + bT \tag{2.2}$$

Where ρ is the density in [kg · m^{-3}], T the temperature in [K] and a, and b are fitting parameters. These parameters are obtained via a fit of the experimental data, shown in Table 2.2.

Table 2.2: Fitting parameters of the linear equation for the density as depicted in equation 2.2.

DES	a $[\mathrm{kg} \cdot \mathrm{m}^{-3}]$	b $[\mathrm{kg} \cdot \mathrm{m}^{-3} \cdot \mathrm{K}^{-1}]$
DecA:$N_{4444}-Cl$ (2:1)	1105.34	-0.63
DecA:$N_{8881}-Br$ (2:1)	1139.30	-0.66
DecA:$N_{8881}-Cl$ (2:1)	1084.29	-0.63
DecA:$N_{7777}-Cl$ (2:1)	1082.04	-0.64
DecA:$N_{8888}-Br$ (2:1)	1124.18	-0.65
DecA:$N_{8888}-Cl$ (2:1)	1077.32	-0.63

There are several (semi)-empirical expressions to quantify the temperature dependence of the (shear) viscosity. Here, the Vogel-Fulcher-Tammann equation is applied since it is often used to describe the variation of viscosities over temperature for ILs.[88,89] The Vogel-Fulcher-Tammann equation reads:

$$\eta = A_\eta \cdot \exp \frac{B_\eta}{T - C_\eta} \tag{2.3}$$

Where η is the viscosity in $[\mathrm{mPa} \cdot \mathrm{s}]$, T is the temperature in [K] and A_η $[\mathrm{mPa} \cdot \mathrm{s}]$, B_η [K] and C_η [K] are the fitting parameters. The obtained parameters are depicted in Table 2.3.

Table 2.3: Fitting parameters of the Vogel-Fulcher-Tammann (Equation 2.3).

DES	A_η $[\mathrm{mPa} \cdot \mathrm{s}]$	B_η [K]	C_η [K]
DecA:$N_{4444}-Cl$ (2:1)	0.033	1267.18	-157.17
DecA:$N_{8881}-Br$ (2:1)	0.111	1087.44	-171.01
DecA:$N_{8881}-Cl$ (2:1)	0.202	949.49	-183.14
DecA:$N_{7777}-Cl$ (2:1)	0.069	1138.60	-152.82
DecA:$N_{8888}-Br$ (2:1)	0.020	1647.57	-139.02
DecA:$N_{8888}-Cl$ (2:1)	0.043	1372.65	-150.58

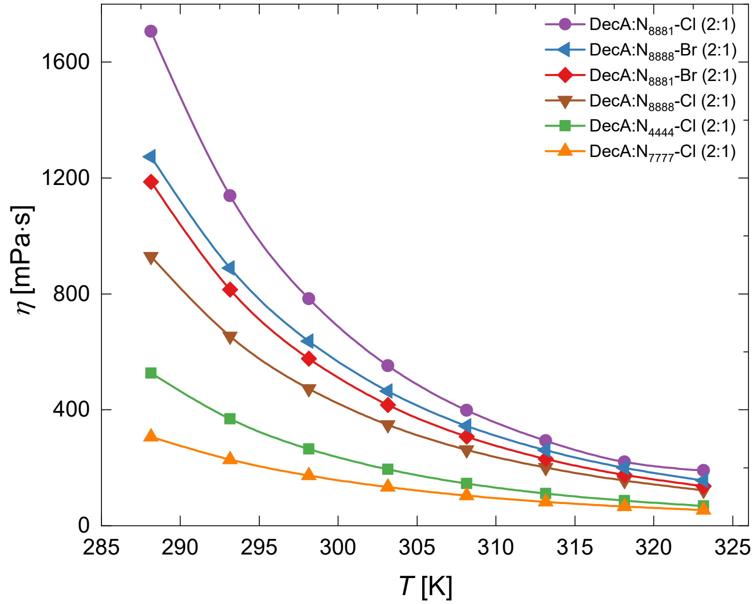


Figure 2.4: Temperature dependence of the shear viscosity for various DESs. The lines are added for clarification purposes.

2.3.3 Cross-contamination between the DES and water phase

An important aspect when working with a two-phase system of a hydrophobic solvent and water is the cross-contamination. It was investigated how much DES transfers to the water phase and vice versa. Since decanoic acid has a low solubility in the water phase, the transfer of DES to the water phase was based on the quaternary ammonium salts. It was expected that DecA:$N_{4444}-Cl$ (2:1) had the most cross-contamination, since it had the shortest carbon chains. Analysis of the DES phase after mixing with water showed an increase of the water content in the DES phase from approximately 0.81 wt % to 6.94 wt %. Ion chromatography (IC) showed that around 34.8 % $\left(m_{\text{salt,leached/msalt,DES}}\right)$ of the $N_{4444}-Cl$ leached to the water phase, a phenomena that occurs due to the high solubility of $N_{4444}-Cl$ in water.

The leaching of the quaternary ammonium salts into the water phase was confirmed using ^{1}H-NMR spectroscopy of the top (DES rich) phase (appendix 2.5.2). For comparison the DESs before mixing with water were also analyzed. The molar ratio obtained from NMR between the DecA (peak at 2.1 ppm) and specific peaks of the quaternary ammonium salt (peak at 3.1 ppm) was calculated for all DESs, before and after mixing with water. A deviation from the expected ratio, before mixing, gives indication of possible occurrence of reactions between the components, while a deviation after mixing, indicates leaching of (one) the components to the water phase.

For the DecA:$N_{4444}-Cl$ DES prepared in the theoretical molar ratio of 2:1, upon comparing Figure 2.6 and Figure 2.7, the estimated molar ratio between the integrals of the peaks at position 2.1 ppm (for DecA) and 3.1 ppm (for $N_{4444}-Cl$) is 2.07:1 before mixing with water, while after mixing a ratio of 1.08:1 was found. This indicates that no reaction occurred between the components, but after mixing with water, approximately 49% of the $N_{4444}-Cl$ leached to the water phase. This value is even higher than the one obtained from the IC analyses and clearly shows that there is an extensive transfer of this particular salt to the water phase, as expected. Based on similar calculations from the NMR spectra (appendix 2.5.2) no reaction between the components or leaching of the salt was detected for all the other DESs.

Table 2.4: Cross contamination values between the DES and water phase. The water contents correspond to the DES mixing with water. C_{salt} is the salt concentration in the water-rich phase after mixing the DES with water. $m_{salt,leached/msalt,DES}$ is the mass fraction of quaternary ammonium salt that leached to the water phase.

DES	w_{after,H_2O} [wt%]	C_{salt} [mg_{salt}/g_{water}]	$(m_{salt,leached/msalt,DES})$ [$g \cdot g^{-1}$]
DecA:$N_{4444}-Cl$ (2:1)	6.94	155.21	0.3475
DecA:$N_{8881}-Br$ (2:1)	4.24	13.08	0.0231
DecA:$N_{8881}-Cl$ (2:1)	6.22	16.19	0.0300
DecA:$N_{7777}-Cl$ (2:1)	2.34	13.09	0.0232
DecA:$N_{8888}-Br$ (2:1)	2.00	14.23	0.0523
DecA:$N_{8888}-Cl$ (2:1)	1.78	11.44	0.0193

To reduce the solubility in water of the quaternary ammonium based DESs, quaternary ammonium salts with higher hydrophobicity were investigated. The quaternary ammonium salts $N_{8881}-Br$ and $N_{8881}-Cl$ as HBA were studied. It was anticipated that these quaternary ammonium salts were more hydrophobic due their longer carbon chains. For $N_{8881}-Br$ it was shown that only 2.3 % leached to the water phase, while this was 3.0 % for $N_{8881}-Cl$. This is more than an order of magnitude smaller than the leaching of $N_{4444}-Cl$. Nevertheless, this is still a concentration in the water phase that needs to be recovered. The water contents of the DES prepared with $N_{8881}-Br$ and $N_{8881}-Cl$ after mixing with water increased to 4.24 and 6.22 wt %, respectively. These are slightly lower than the water content of DecA:$N_{4444}-Cl$ (2:1) but still rather high. It was anticipated that this was caused by the non-symmetrical shape of the quaternary ammonium salt $N_{8881}-Cl$, inducing less steric hindrance for the water to have contact with the charged groups at the methyl group.

Since these results were not satisfactory, it was decided to shift to quaternary ammonium salts with alkyl chain lengths of 7 or 8 carbon atoms. These DESs were expected to be more hydrophobic due to the longer alkyl chains and the symmetrical shape of the cation. This is related to the enhancement of the steric hindrance avoiding the accessibility of water to the charged core of the salt. The DESs DecA:$N_{4444}-Cl$ (2:1), DecA:$N_{8888}-Br$ (2:1) and DecA:$N_{8888}-Cl$ (2:1) contained water contents, after mixing, of 2.34, 2.00 and 1.78 wt %, respectively. These were results as expected, since the carbon chains of ($N_{7777}-Cl$) are shorter than those of the octyl based quaternary ammonium salt and Cl^- is slightly more hydrophobic than Br^-. A different trend is observed for the leaching; salts with the anion Cl^- have less transfer to the water-rich phase. As mentioned previously, it is hypothesized that the Cl^- is more hydrophobic than Br^-.

2.3.4 Application: extraction of volatile fatty acids

It was verified whether the prepared hydrophobic DESs could be used for the extraction of the volatile fatty acids (VFAs) acetic, propionic and butyric acid from diluted aqueous solutions. Amine-based extractants, e.g. trioctylamine (TOA), are conventionally used for the extraction of carboxylic acids.[90] Usually, these long-chain aliphatic amines are dissolved in water-immiscible diluents, such as octanol, in order to increase their extracting power. In this work, pure TOA was used as extractant in order to compare with the newly prepared hydrophobic DESs. A solution of 1 wt % of VFA in water (2 mL, pH = 3.3) was brought in contact with DES/TOA (2 mL) during 2 h, after which both phases settled in a centrifuge for 30 min and the phases were analyzed with high performance liquid chromatography (HPLC). A more detailed description of the extraction procedure together with the adopted methodology can be found in paragraph 2.2.1. The distribution coefficient of the DESs and of the pure TOA for each VFA at room temperature are listed in Table 2.5.

Table 2.5: Distribution coefficients at room temperature of acetic, propionic and butyric acids from diluted aqueous solutions with the reported DESs and trioctylamine as reference. The calculation of the distribution coefficient is given in Equation 2.1.

DES	Acetic acid	Propionic acid	Butyric acid
DecA:$N_{8881}-Br$ (2:1)	0.30	0.63	0.83
DecA:$N_{8881}-Cl$ (2:1)	0.38	0.71	0.90
DecA:$N_{7777}-Cl$ (2:1)	0.32	0.77	0.92
DecA:$N_{8888}-Br$ (2:1)	0.31	0.66	0.87
DecA:$N_{8888}-Cl$ (2:1)	0.25	0.53	0.81
Trioctylamine	0.19	0.46	0.74

The studied hydrophobic DESs show higher extraction efficiencies for the VFAs compared to TOA. Due to the hydrogen accepting ability of the quaternary ammonium salt, the DES favors the extraction of VFAs. When hydrophobic DESs are used as extractants, the extraction efficiency increases with the alkyl chain length of the VFA, due to the increase of the dispersive interactions between the used solvents and the VFAs. The highest extraction efficiencies for all the VFAs were found when using DecA:$N_{8881}-Cl$ (2:1) (asymmetric ammonium) as solvent. This can be related to the lower steric hindrance effect of the alkyl chains, which increases the accessibility not only of the VFAs but also of water. This is in agreement with the lower hydrophobicity of this DES. By replacing $N_{8881}-Cl$ with symmetrical salts (such as $N_{8888}-Cl$ and $N_{7777}-Cl$), the extraction efficiencies decrease with the increase of the alkyl chain of the salt, due to the higher contribution of steric hindrance. Exceptional cases were found for the extraction of propionic and butyric acids using DecA:$N_{7777}-Cl$ (2:1), where higher extraction efficiencies are observed compared to the ones obtained using DecA:$N_{8881}-Cl$ (2:1) as extracting agent. For this DES no proper phase separation could be achieved, the DES was still turbid even after 90 min of centrifugation, which leads to VFAs still present in the DES phase. The difficulties with the separation of the phases might be related with the viscosity of the DES, which hinders the mass transfer and the phase separation.

As previously described for Aliquat 336 and Alamine 336,[91] which are combinations of quaternary ammonium salts, both dissociated and undissociated forms of the acid might be removed, broadening the application of hydrophobic DESs for different pH environments. Yang and co-workers explored the effect of pH on the extraction of acetic, propionic and butyric acids using a tertiary amine (Alamine 336) and a quaternary amine (Aliquat 336).[91] The studied amines had been used as single extractants and were also dissolved in two water-immiscible organic solvents (kerosene and 2-octanol). It was found that Aliquat 336 has the capability of extracting both dissociated and undissociated forms of the acids, whereas Alamine 336 only extracts the dissociated form of the acids.

2.4 Conclusions and outlook

Hydrophobic DESs were developed by combining decanoic acid and quaternary ammonium salts. That the developed DESs are indeed hydrophobic can be concluded from the phase separation between the DES and water, the low water contents after mixing with water ($\sim$1.8 wt %) and the low leaching of the quaternary ammonium salts ($\sim$1.9 wt %). Generally, water content and salt leaching decrease with increasing carbon chain length. The extraction efficiencies increase with increasing chain length, and thus hydrophobicity, of the VFAs. The extraction efficiencies of the VFAs showed that the hydrophobic DESs in all cases perform better than the conventional extraction medium trioctylamine.

Despite that this discovery opens a new field of research, follow-up research should be performed to find more sustainable hydrophobic DESs. Especially aspects as a lower viscosity, easy separation of the two phases and cross-contamination between the DES and water phase should be lowered.

2.5 Appendices

2.5.1 TGA spectra of the DESs

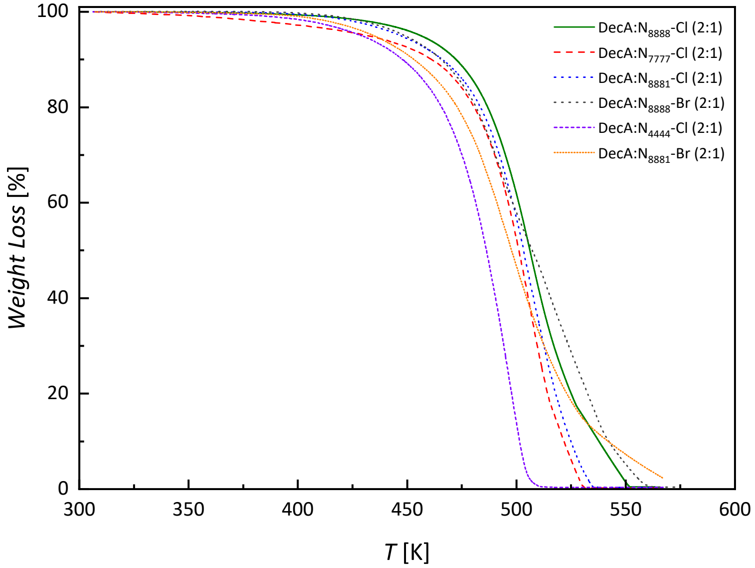


Figure 2.5: TGA curves for all the studied DESs.

2.5.2 NMR spectra of the DESs upon preparation

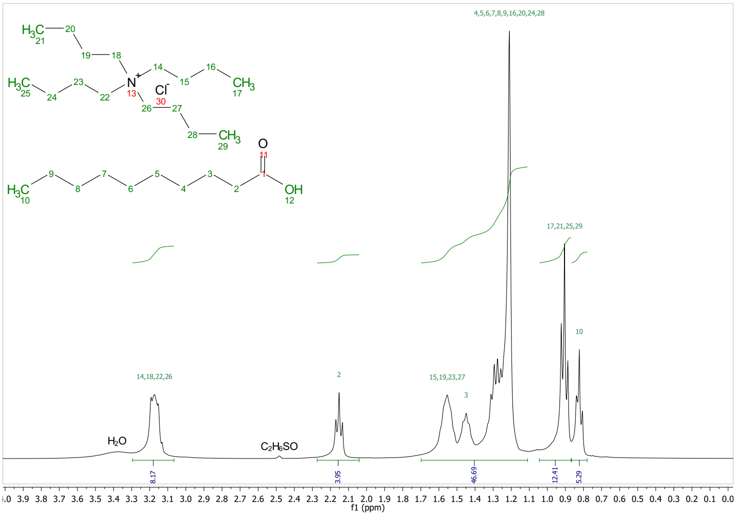


Figure 2.6: ^{1}H-NMR spectrum of DecA:$N_{4444}-Cl$ (2:1) before mixing with water.

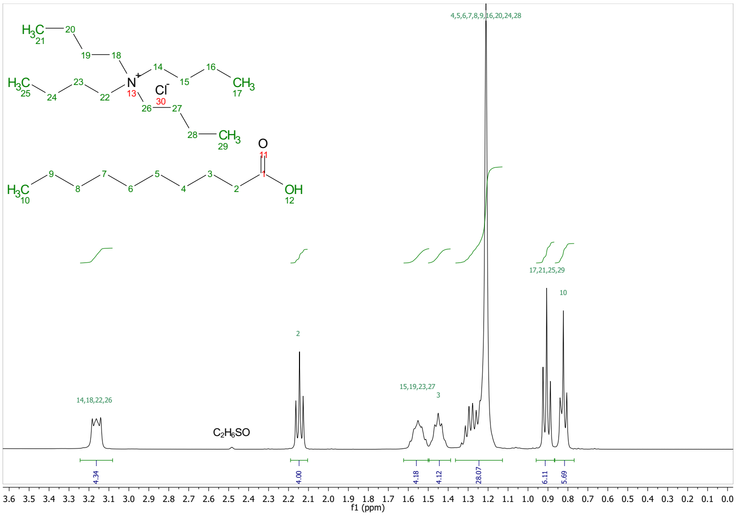


Figure 2.7: ^{1}H-NMR spectrum of DecA:$N_{4444}-Cl$ (2:1) after mixing with water.

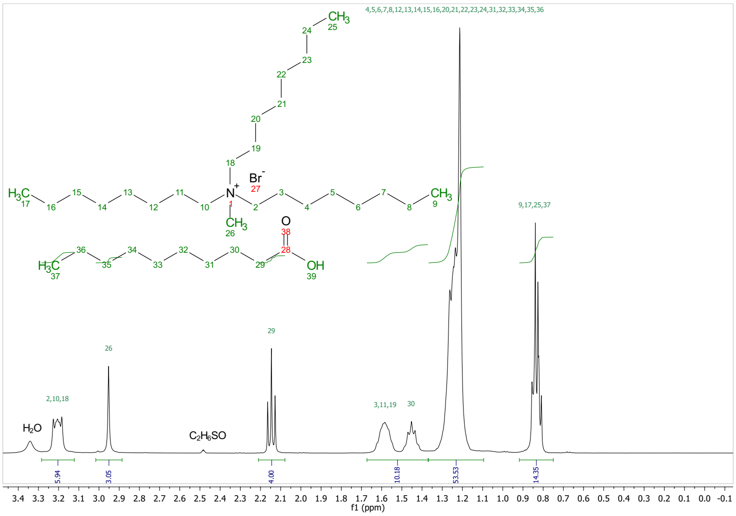


Figure 2.8: ^{1}H-NMR spectrum of DecA:N_{8881} – Br (2:1) before mixing with water.

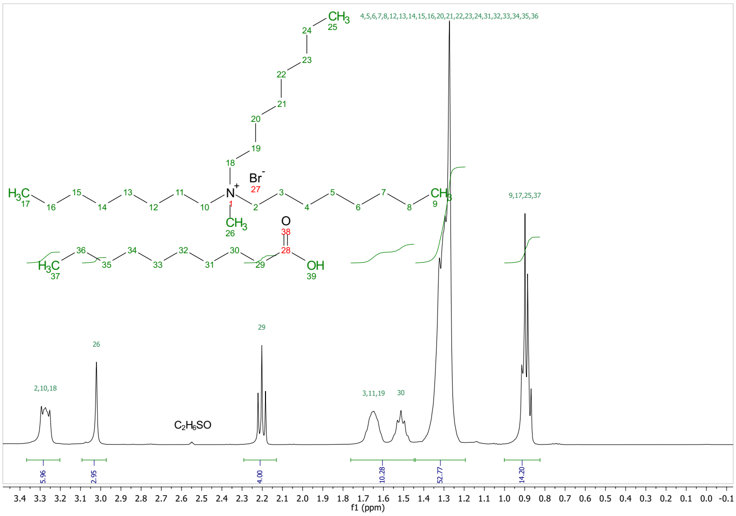


Figure 2.9: ^{1}H-NMR spectrum of DecA:N_{8881} – Br (2:1) after mixing with water.

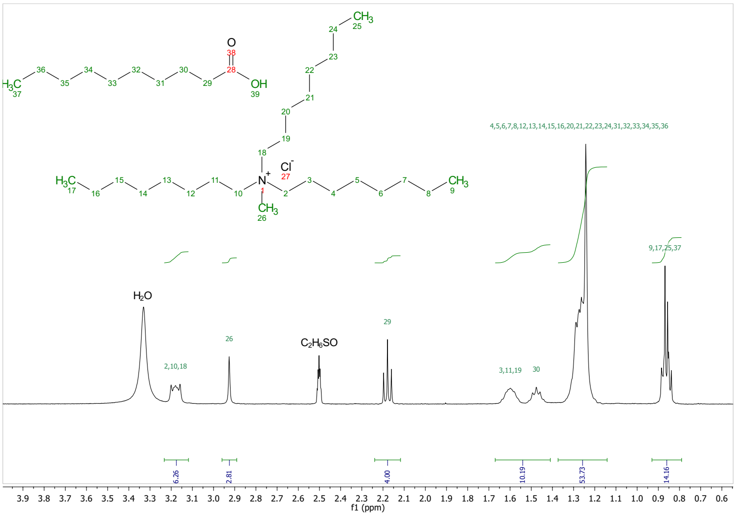


Figure 2.10: ^{1}H-NMR spectrum of DecA:$N_{8881}-Cl$ (2:1) before mixing with water.

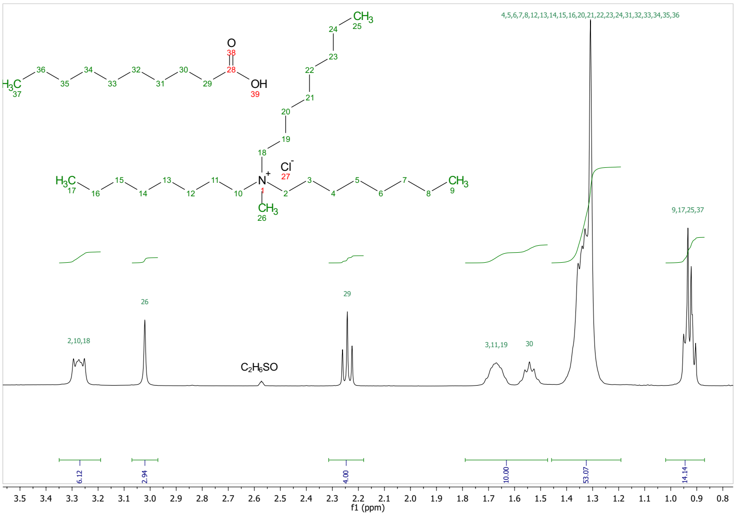


Figure 2.11: ^{1}H-NMR spectrum of DecA:$N_{8881}-Cl$ (2:1) after mixing with water.

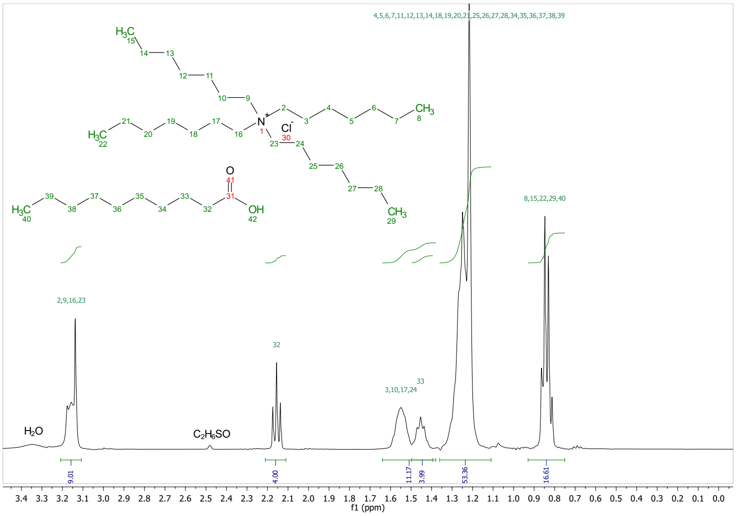


Figure 2.12: ^{1}H-NMR spectrum of DecA:$N_{7777}-Cl$ (2:1) before mixing with water.

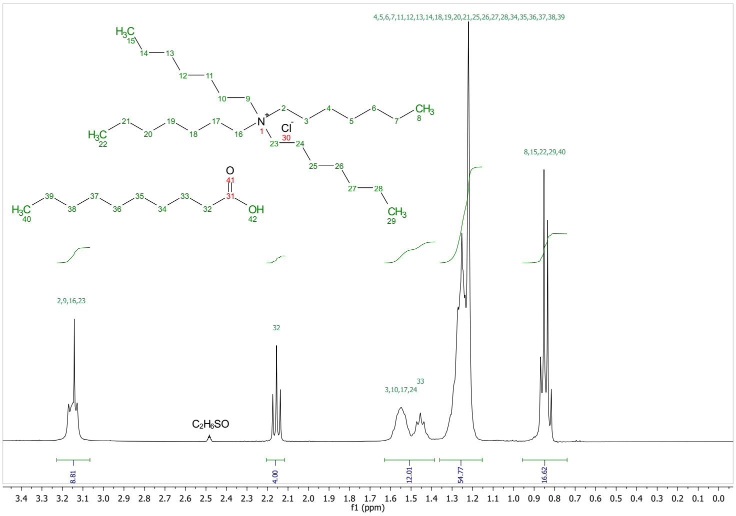


Figure 2.13: ^{1}H-NMR spectrum of DecA:$N_{7777}-Cl$ (2:1) after mixing with water.

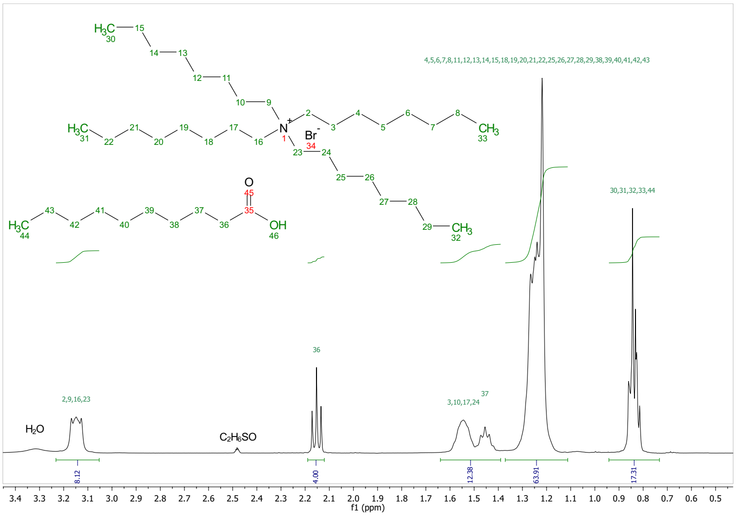


Figure 2.14: ^{1}H-NMR spectrum of DecA:$N_{8888}-Br$ (2:1) before mixing with water.

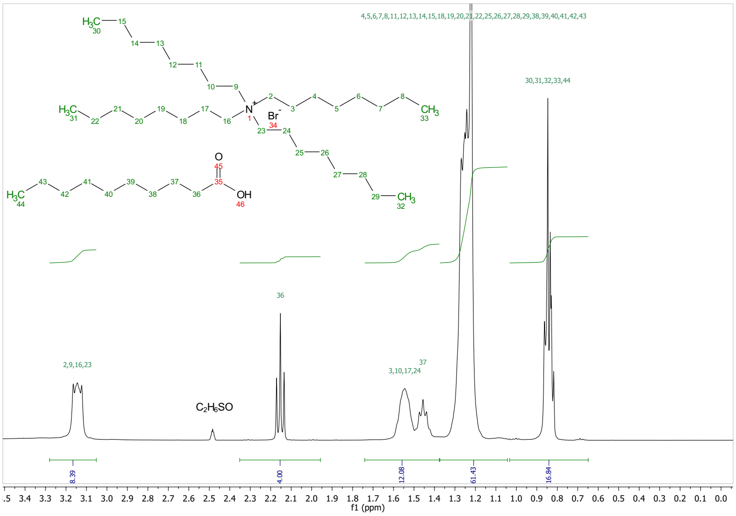


Figure 2.15: ^{1}H-NMR spectrum of DecA:$N_{8888}-Br$ (2:1) after mixing with water.

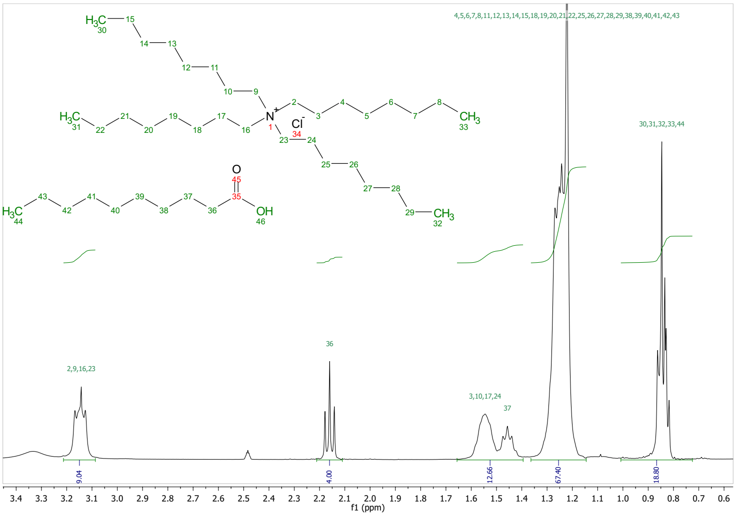


Figure 2.16: ^{1}H-NMR spectrum of DecA:$N_{8888}-Cl$ (2:1) before mixing with water.

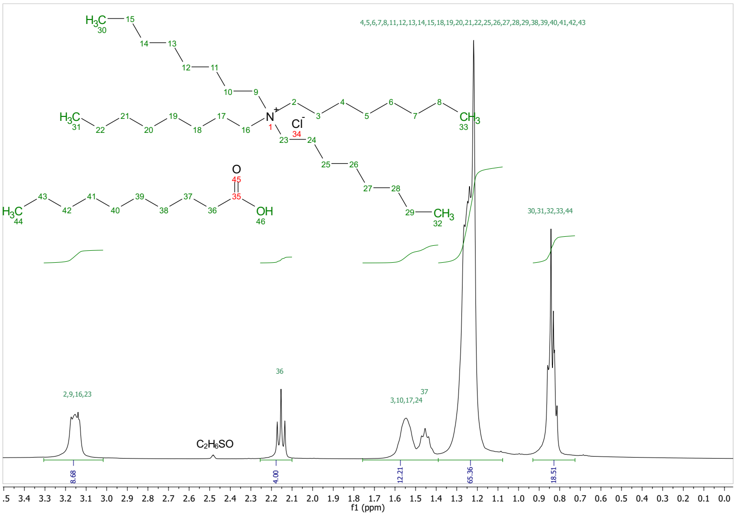


Figure 2.17: ^{1}H-NMR spectrum of DecA:$N_{8888}-Cl$ (2:1) after mixing with water.

2.5.3 FTIR spectra of the DESs

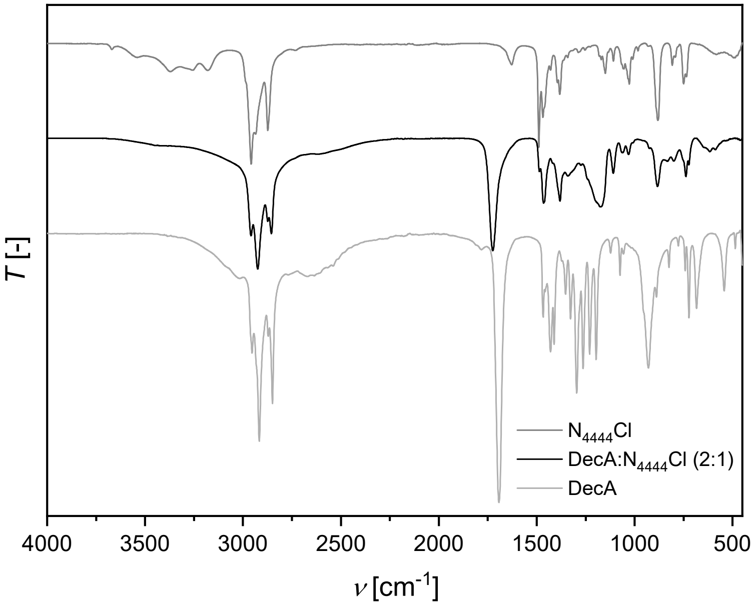


Figure 2.18: Stacked FTIR spectra of DecA:N_{4444}–Cl (2:1) and its starting components.

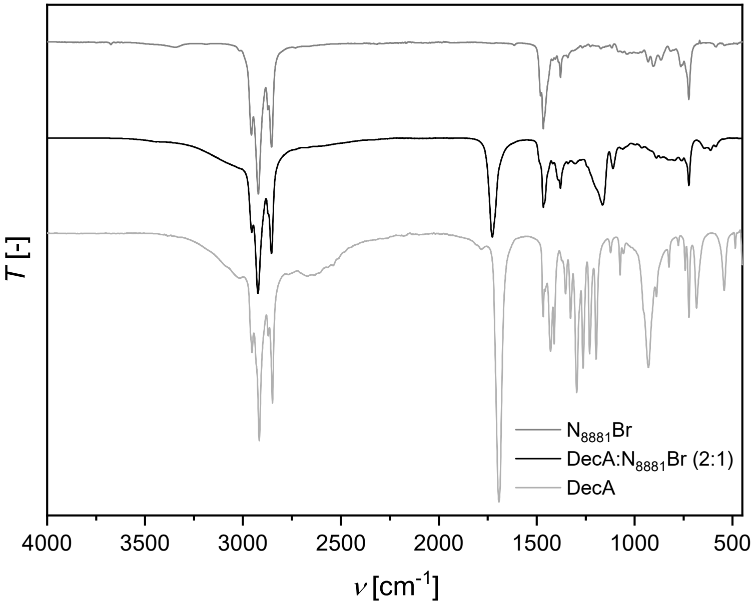


Figure 2.19: Stacked FTIR spectra of DecA:N_{8881}–Br (2:1) and its starting components.

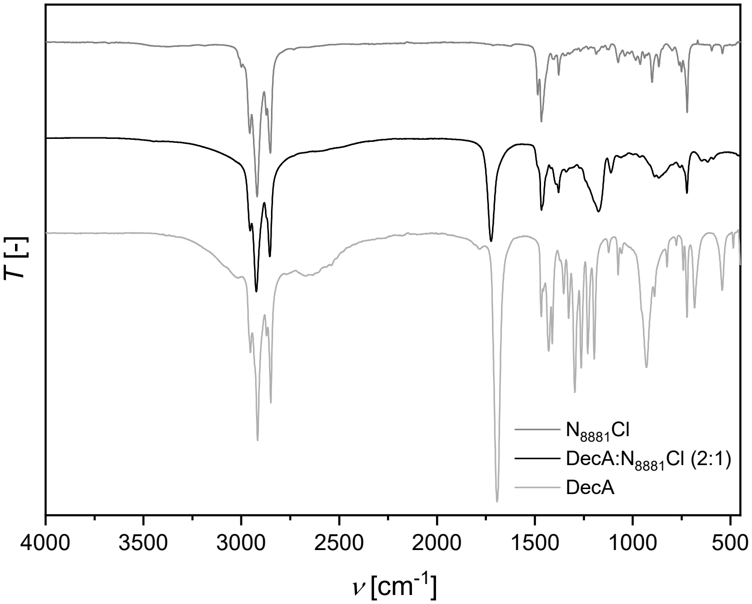


Figure 2.20: Stacked FTIR spectra of DecA:N_{8881}−Cl (2:1) and its starting components.

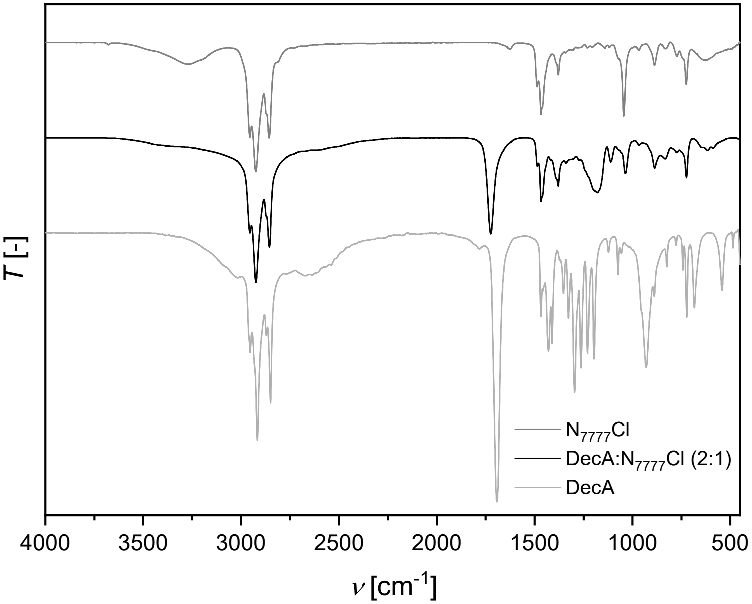


Figure 2.21: Stacked FTIR spectra of DecA:N_{7777}−Cl (2:1) and its starting components.

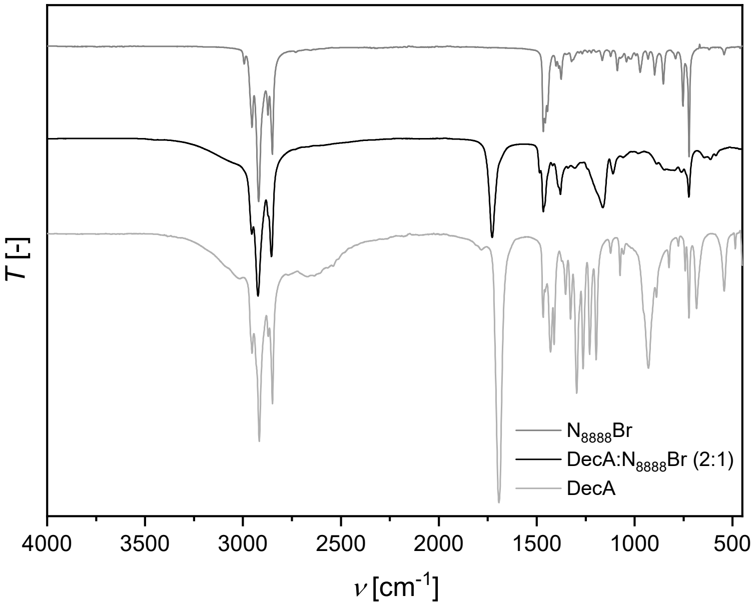


Figure 2.22: Stacked FTIR spectra of DecA:$N_{8888}-Br$ (2:1) and its starting components.

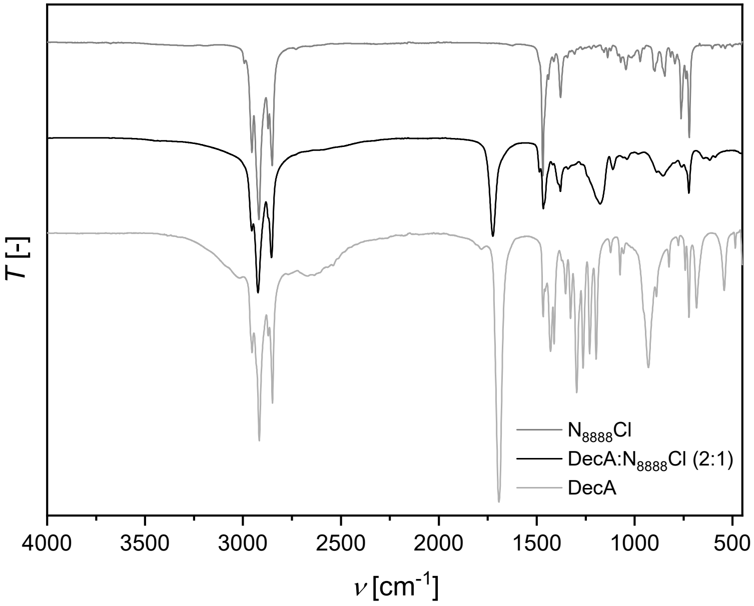


Figure 2.23: Stacked FTIR spectra of DecA:$N_{8888}-Cl$ (2:1) and its starting components.

Chapter 3

A Search for Sustainable Hydrophobic Deep Eutectic Solvents

Abstract

The aim of this work is the identification and characterization of hydrophobic deep eutectic solvents (DESs), based on terpenes. 507 combinations of solid components are tested, which results in the identification of 17 new hydrophobic DESs. Four criteria are introduced to assess the sustainability of these hydrophobic DESs, i.e. a viscosity at least lower than $100\,\mathrm{mPa \cdot s}$, a density difference between DES and water of at least $50\,\mathrm{kg \cdot m^{-3}}$ upon mixing of the DES and water, low transfer of the DES to the water phase and minor to no pH change. The results show that five new hydrophobic DESs; Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2) and 1-tdc:Men (1:2), satisfy these criteria and thus are promising hydrophobic DESs. These new DESs can be considered as natural deep eutectic solvents, which are commonly accepted as environmentally friendly. A selected group of the hydrophobic DESs were used for the extraction of riboflavin from water. They show higher removal of riboflavin in comparison to decanoic acid:tetraoctylammonium bromide (2:1) (see Chapter 2).

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3.1 Introduction

In the near future, conventional solvents should be replaced by designer solvents to obey the 12 principles of Green Chemistry, introduced by Anastas and Warner.[4] Currently, the best studied designer solvents have been ionic liquids (ILs), which are defined as salts that consist of a cation and an anion with a melting temperature lower than that of water, preferably lower than room temperature.[5] Advantages of ILs over conventional solvents include their low volatility, their ability to tune their physicochemical properties by selecting different constituting components, good solvability for a wide range of organic and inorganic solutes and high polarity due to their poor coordination of the ions.[5] Thus, ILs provide a strong alternative for conventional solvents in both one and two-phase systems, but their wide exploitation is still hindered by the very high production costs and their possible toxicity.[92,93]

In 2003 another class of designer solvents, called deep eutectic solvents (DESs), were reported. The first DESs reported in literature were composed of combinations of amides and choline chloride.[94] DESs consist of two or more components, which most likely interact via hydrogen bonding and Van der Waals interactions.[57,58] These physical interactions are supposed to induce a dramatic decrease in the melting temperature of the mixture, as opposed to the melting temperature of the pure components, by stabilizing the configuration of the liquid. DESs have similar advantages as ILs, but overcome their disadvantages such as their expensive synthesis and purification.

DES research initially focused on hydrophilic DESs. In 2015 hydrophobic DESs were reported in the literature for the first time, see Chapter 2. These were tested for the extraction of volatile fatty acids (VFAs) and biomolecules, such as caffeine and vanillin, from an aquatic environment.[79,95] Although the field of hydrophobic DESs is new, already quite some papers about their use were published. These include the removal of metal ions,[80,96] furfural and hydroxymethylfurfural by the use of membrane technology,[81] and pesticides from H_2O.[20] Furthermore, hydrophobic DESs were applied to study CO_2 capture,[97,98] and their use for microextractions was investigated.[82,83] Moreover, the extraction of components from leaves using hydrophobic DESs was studied.[84,85]

The hydrophobic DESs currently presented in the literature are promising, especially application-wise, but several improvements are needed. These include lowering the cross contamination of the DES and water phase when used for extraction. Furthermore, the constituents of the DES should be more sustainable, e.g. biodegradable, non-toxic and non-volatile, to ensure the production of truly 'green' hydrophobic DESs.

This chapter describes the investigation on the search for and characterization of new hydrophobic DESs that are more sustainable, achieved by overcoming the disadvantages of the small group of currently available ones. For this reason, a group of plant extracts called terpenes were selected for this research to investigate their ability to form eutectic liquid mixtures. Recently, terpenes showed great promise for the formation of eutectics. The combination of these components can be considered as natural deep eutectic solvents (NADES), which are generally accepted as environmentally friendly.[72,99] The following components were used as DES constituents in this work: decanoic acid (DecA), dodecanoic acid (DodE), menthol (Men), thymol (Thy), 1-tetradecanol (1-tdc), 1,2-decanediol (1,2-dcd), 1-10-decanediol (1,10-dcd), cholesterol (Chol), trans-1,2-cyclohexanediol (1,2-chd), 1-napthol (1-Nap), atropine (Atr), tyramine (Tyr), tryptamine (tryp), lidocaine (Lid), cyclohexanecarboxaldehyde (Chcd), caffeine (Caf) and coumarin (Cou). Some components were used as hydrogen bond donors (HBDs), while others were used as hydrogen bond acceptors (HBAs). A few of these components can both donate and accept hydrogen bonds. Some of the combinations with lidocaine, shown in Table 3.2, were previously presented in the literature as eutectic mixtures.[100–102] Since there is no proper definition and boundary conditions for DESs, these binary mixtures containing lidocaine were considered as DESs.

To investigate the sustainability of these hydrophobic DESs four parameters are investigated: the viscosity, the density, pH of the water phase and the amount of organics that is transferred to the water phase coexisting with the DES. Density and viscosity values are selected as relevant criteria because these quantities have an influence on the separation behavior of the DES and H_2O phase and determine the amount of energy needed to pump these fluids. For ease of processability, the viscosity should be as low as possible, while the difference of the density between the DES and water should be as large as possible. To accelerate the extraction process, the amount of DES that is transferred to the water phase and the pH are chosen since cross contamination of water and DES phase should be minimized. There should be a limited change in pH, because the amounts of the DES that transfers to the water phase should be as low as possible. Ideally, the components of the DESs should also be cheap, biodegradable and non-toxic. To account for the points of biodegradable and non-toxic aspects of hydrophobic DESs, terpenes are chosen as components. In this chapter the focus is on several physical-chemical properties of the new DESs. More detailed investigations on their sustainability and toxicity should be further addressed with specific methods as stated in the literature,[69,70,103] even as these DESs based on natural components are generally accepted as environmentally friendly.[72,99] Next to the main criteria before mixing, water contents and thermogravimetric analysis (TGA) are measured. Nuclear magnetic resonance (NMR) of the DES is performed to investigate whether the DES remains an unreacted mixture.

To investigate the application potential of these hydrophobic DESs their capability to extract compounds from the water phase is studied. Riboflavin (vitamin B2) was chosen because it is an essential vitamin and it is not easy to extract from aqueous solutions. The results of the novel hydrophobic DESs presented in this study are compared to the hydrophobic DES composed of decanoic acid and tetraoctylammonium bromide in a 2:1 molar ratio, which is one of the first hydrophobic DESs presented in the literature.

3.2 Experimental section

3.2.1 Materials and preparation

Materials

All chemicals were ordered from Sigma-Aldrich, expect for riboflavin which was purchased from TCI Chemicals. Their purities (as stated by the supplier) and CAS numbers are depicted in Table 3.1 .

Table 3.1: Components that were used in this investigation with their purities (as stated by the supplier).

Component	CAS	Purity [wt%]
Decanoic acid (DecA)	334-48-5	≥ 98
Dodecanoic acid (DodE)	143-07-7	≥ 99
Menthol (Men)	89-78-1	≥ 99
Thymol (Thy)	89-83-8	≥ 99
1-tetradecanol (1-tdc)	112-72-1	≥ 97
1,2-decanediol (1,2-dcd)	1119-86-4	≥ 98
1,10-decanediol (1,10-dcd)	112-47-0	≥ 98
Cholesterol (chol)	57-88-5	≥ 92.5
trans-1,2-cyclohexanediol (1,2-chd)	460-57-7	≥ 98
1-Napthol (1-Nap)	90-15-3	≥ 99
Atropine (Atr)	51-55-8	≥ 99
Tyramine (Tyr)	51-67-2	≥ 98
Tryptamine (Tryp)	61-54-1	≥ 98
Lidocaine (Lid)	137-58-6	$\geq$ N.A.
Cyclohexanecarboxaldehyde (Chcd)	2043-61-0	≥ 97
Caffeine (Caf)	58-08-2	≥ 98
Coumarin (Cou)	91-64-6	≥ 99
Riboflavin	83-88-5	$\geq$ N.A.

Preparation of the hydrophobic DESs

The formation of hydrophobic DESs was tested by mixing two solid components at three different molar ratios, e.g. 2:1, 1:1 and 1:2, with a total weight of 2 g. A Mettler Ax205 balance with an uncertainty of 20 µg was used for weighing the chemicals. The first component was weighed directly in the flask, in which a magnetic stirrer was already present. The second component was first weighed on a weighing boat, after which the correct amount was transferred into the flask. The components in the flask were premixed on a VWR Analog Vortex Mixer and heated in a metal heating block. An IKA RCT basic was used for monitoring the stirring speed and temperature. An IKA ETS-D5 temperature controller with an uncertainty of ± 0.1 K was used for temperature control.

The formation of the hydrophobic DESs was investigated via a standard procedure. After preparation and premixing, the flasks were heated and stirred for 2 h at a temperature of approximately 313 K. In case a homogenous liquid sample was produced, the flask was kept at room temperature for 24 h to check its stability. The sample was considered a DES if no crystals were visually present in the liquid after 24 h. The samples that formed no liquid were further heated to 333.15 K. The same procedure as explained before was used. If no liquid was formed at 333.15 K the temperature was heated to 353.15 K, after which the same procedure was used.

The combinations of components that formed a DES on the 2-gram scale, were scaled up to form 50 g of DES. For the 50-gram scale it was investigated whether the DESs were also formed at room temperature. Only the DESs that were also stable at a 50-gram scale were further analyzed. During the analyses, crystals appeared in some DESs within the timeframe of a month. Those DESs were discarded from the investigation and not further analyzed.

Mixing with water

18.0 g of MilliQ water was weighed in a 50 mL Centrifuge tube (CELLSTAR®), after which 18.0 g of hydrophobic DES was added. Proper mixing was induced via an IKA KS 4000 I incubating shaker (500 RPM, RT). After shaking, the DES and water phase were separated via centrifugation with a Sigma 2-16 KL centrifuge. The DESs DecA:Men (1:1), DecA:Men (1:2), Men:Lid (2:1), Thy:Lid (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Lid (1:1), Thy:Cou (1:1), Thy:Men (1:2), 1-tdc:Men (1:2), 1,2-dcd:Thy (1:2), 1-Nap:Men (1:2) were centrifuged for 10 min at 6000 RPM, while the DESs DecA:Lid (2:1), DecA:Atr (2:1), DodE:Lid (2:1), DodE:Atr (2:1) and Atr:Thy (1:2) were centrifuged for 60 min at 12.000 RPM. After centrifugation, the DES and water phase were taken with a needled syringe. For the DESs DodE:Lid (2:1) and DodE:Atr (2:1) no proper phase separation could be achieved. Thus, these were excluded from analysis after mixing with H_2O.

3.2.2 Analytical methodologies

Water content

The water contents of the DESs were measured with a Mettler Toledo D39 Karl Fischer titration apparatus (coulometer). The DESs DecA:Lid (2:1) and DecA:Atr (2:1) had a high water content (>10 wt%) and could not be properly measured on the Toledo equipment. Those samples were measured on a Metrohm type 899 coulometer. The coulometers were filled with 20 mL chloroform and 80 mL Hydranal Coulomat AG. The DES 1-Nap:Men (1:2) could not be measured on a coulometric Karl Fischer, so it was measured on a volumetric Karl Fischer apparatus. A Metrohm type 795 KFT volumetric Karl Fischer was used. Before use of the Karl Fischer apparatuses, they were checked with water standards of 0.01, 0.1 and 1.0 wt% of water.

Viscosity and density

The measured physicochemical properties of the hydrophobic DESs are the density and the viscosity. The density was determined with an Anton-Paar DMA 4500 M with a deviation of the density of $\pm$ 0.05 $\mathrm{kg \cdot m^{-3}}$ and a temperature variation of ± 0.05 K. The discrepancy of the density from the several reference oils that were measured was not more than $\pm$ 0.01 $\mathrm{kg \cdot m^{-3}}$. The viscosity was measured with an Anton Paar Lovis 2000 ME rolling ball viscometer. All hydrophobic DESs, except for Atr:Thy (1:2), were measured in a glass capillary with an inner diameter of 1.8 mm equipped with a gold-coated ball. The coefficient of variation was below 0.2%, while the forward/backward deviation was at its most 1.0%. The capillary was calibrated with a N26 synthetic base oil, which was supplied by Paragon scientific ltd. For the DES Atr:Thy (1:2) the viscosity measurement before mixing was performed on an Anton Paar Physica MCR 301 rheometer, because of its high viscosity. A concentric cylinder system (CC27) was used. The inner diameter is 26.66 mm, while the outer diameter is 28.92 mm. Measurements and calibration were performed as presented elsewhere.[81] After mixing with H_2O, the capillary of 2.5 mm was used for Atr:Thy (1:2), also equipped with a gold-coated ball. The variation coefficient for this capillary was below 0.5%, while the forward/-backward deviation was at most 1.0%. The capillary was calibrated with a N100 synthetic base oil.

Thermogravimetric analysis (TGA)

The decomposition temperatures of the DESs were measured with a TGA Q500 from TA Instruments. The weight accuracy is 0.1%, while the temperature accuracy is 1 K. A heating rate of $10\,\mathrm{K}\cdot\mathrm{min}^{-1}$ was used from 298.15 to 873.15 K. The degradation temperature is the weight loss onset temperature determined via the step tangent method. The thermograms were analyzed with the TA Instruments Universal Analysis 2000 software (version 4.5A, Build 4.5.0.5).

Nuclear magnetic resonance (NMR)

Both proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) were performed. A Bruker 400 automatic NMR was used with 128 scans and a relaxation time of 3 s for the ^{1}H and 1000 scans with a relaxation time of 3 s for the ^{13}C. 8″ Wilmad NMR tubes with an outside diameter of 5 mm were used for the measurements, in which DES diluted with chloroform was added. Analysis of the spectra was conducted with Mestrenova (version v11.0.4-18998) and ChemBiodraw (version 348-208690-1653).

For the analysis of the ^{1}H NMRs it was checked whether all peaks of the protons were in the theoretical molar ratio to investigate whether no reactions between the components of the DES occurred. Therefore, the integral of a specific peak of the molecule used as HBD was compared to the integral of a specific peak for the molecule used as HBA. For the ^{13}C NMRs it was checked whether extra peaks were present, which is an indication of reactions between the two components of the DES.

pH of the water whase after mixing the DESs with water

The pH of the water phase was measured with a Mettler Toledo seven compact pH/Ion meter (S220). A 5 point calibration was performed in the range of a pH of 2 to 7. Standards with higher pH, up to a pH of 10, were tested for calibration and also gave adequate results. The pH measuring range of the meter is from -2 to 20. The pH accuracy is $\pm$ 0.002, while the accuracy of the temperature is $\pm$ 0.5 K. The probe connected to the pH meter is an InLab Micro 51343160.

Total Organic Content (TOC)

The total organic carbon (TOC) of the water phase was determined by a Shimadzu TOC-L CPH/CPN with auto sampler ASI-L (24 mL vails). The amount of TOC was calculated by two calibration curves (0-10 ppm and 0-100 ppm). The vial was filled with a 100 times diluted sample and 0.5 wt% $1\,\mathrm{mol} \cdot \mathrm{L}^{-1}$ hydrochloric acid was automatically added before injection. The injection volume was set to $50\,\mu\mathrm{L}$. The TOC amount was measured in duplicate with an uncertainty $<$1.5%.

NMR of the water phase

The molar ratio between the two components of the hydrophobic DES that transferred to the water phase was investigated with ^{1}H NMR. After mixing water with the DES, a sample of the water phase was taken and added to a Wilmad-LabGlass 528-pp-7 tube containing a coaxial insert (Wilmad- LabGlass WGS-5BL) with D_2O. The measurements were performed with a Bruker 400 automatic NMR and the water peak was suppressed, by using the software program Bruker NMR. A relaxation time of 3 s was used and 100 scans were performed. This adjustment allowed analyzing the spectra of the low concentrated DESs in the water phase, as follows. The ^{1}H NMR spectra showed the protons of the components of the hydropobic DES present in the water phase. Well defined peaks of the HBD and HBA were integrated. By dividing the integral of specific peaks obtained for the HBD and HBA component, the molar ratio at which the two components of the DES were present in the water phase could be estimated. The localization of the DES components peaks in the water phase was based on the NMRs of the pure components in $CDCl_3$. The results showed a standard deviation within the same molecule of approximately 10%.

3.3 Results and discussion

The tested combinations for this search are presented in Table 3.2, where the molecules expected to behave as hydrogen bond donors (HBDs) are depicted on the left side (first column) and the hydrogen bond acceptors (HBAs) on top (first row). Ratios of 2:1, 1:1 and 1:2 between the HBD and HBA were chosen and all ratios were tested on a 2 gram scale. Components that formed no DESs are excluded. Of the 507 initial experiments, 29 mixtures liquefied upon mixing and leaving the samples at room temperature for 24 h, which at that point were assumed to be hydrophobic DESs (green cells in Table 3.2).

From these expected hydrophobic DESs a batch of 50 gram was produced, of which some of them showed some minor to major crystal formation on the bottom of the glass after storage for some time (up to 30 days). These were excluded from the screening, which resulted in a final amount of 17 hydrophobic DESs that were further investigated. These are: DecA:Lid (2:1), DecA:Atr (2:1), DecA:Men (1:1), DecA:Men (1:2), DodeE:Lid (2:1), DodE:Atr (2:1), Men:Lid (2:1), Thy:Lid (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Lid (1:1), Thy:Cou (1:1), Thy:Men (1:2), 1-tdc:Men (1:2), 1,2-dcd:Thy (1:2), 1-Nap:Men (1:2) and Atr:Thy (1:2).

Table 3.2: Combination of substances that formed liquids (marked cells) on a 2 g scale. Components that formed no liquid with another substance were excluded from the table.

	HBA	Men	Lid	Thy	Atr	Cou
HBD	ratio					
DecA	2:1		🟩		🟩	
DecA	1:1	🟩	🟩	🟩		
DecA	1:2	🟩		🟩		
DodE	2:1		🟩		🟩	
DodE	1:1		🟩			
DodE	1:2					
Men	2:1		🟩			
Men	1:1					
Men	1:2					
Thy	2:1		🟩			🟩
Thy	1:1		🟩			🟩
Thy	1:2	🟩				
1-tdc	2:1					
1-tdc	1:1					
1-tdc	1:2	🟩		🟩		
1,2-dcd	2:1					
1,2-dcd	1:1			🟩		
1,2-dcd	1:2	🟩		🟩		
1,10-dcd	2:1					
1,10-dcd	1:1			🟩		
1,10-dcd	1:2			🟩		
1-Nap	2:1					
1-Nap	1:1					🟩
1-Nap	1:2	🟩				
Atr	2:1					
Atr	1:1					
Atr	1:2			🟩		
Tryp	2:1					
Tryp	1:1			🟩		
Tryp	1:2			🟩		

3.3.1 Densities and viscosities

Of the 17 hydrophobic DESs selected, the water contents, densities and viscosities were measured after preparation, which are presented in Table 3.3.

Table 3.3: Water content, density and viscosity for each hydrophobic DES after preparation. The water contents were measured at room temperature (295 ± 1 K), while the densities and viscosities are measured at 298 K. For the water contents three or four consecutive measurements were performed, while for the densities and viscosites duplicates were measured from the same batch. [1]Measured only once at a shear rate of $43.4\,\mathrm{s}^{-1}$.

DES	Water content [ppm]	ρ [$\mathrm{kg \cdot m^{-3}}$]	η [$\mathrm{mPa \cdot s}$]
DecA:Lid (2:1)	253.8 ± 3.6	961.30 ± 0.005	360.60 ± 0.10
DecA:Atr (2:1)	596.3 ± 14.2	1026.50 ± 0.00	5985.0 ± 7.00
DecA:Men (1:1)	223.3 ± 7.1	899.77 ± 0.030	20.03 ± 0.04
DecA:Men (1:2)	278.6 ± 2.3	899.51 ± 0.010	27.67 ± 0.01
DodE:Lid (2:1)	151.7 ± 2.1	949.50 ± 0.005	370.55 ± 0.15
DodE:Atr (2:1)	478.3 ± 7.4	1008.75 ± 0.005	5599.5 ± 116.50
Men:Lid (2:1)	265.7 ± 2.6	939.18 ± 0.005	68.05 ± 0.08
Thy:Lid (2:1)	255.1 ± 3.2	989.08 ± 0.005	122.05 ± 0.05
Thy:Cou (2:1)	233.0 ± 0.9	1050.47 ± 0.005	31.35 ± 0.01
Thy:Men (1:1)	306.8 ± 4.8	936.56 ± 0.005	53.14 ± 0.00
Thy:Lid (1:1)	296.0 ± 2.5	993.12 ± 0.005	177.15 ± 0.15
Thy:Cou (1:1)	217.3 ± 6.3	1091.80 ± 0.005	29.16 ± 0.03
Thy:Men (1:2)	313.6 ± 4.4	923.84 ± 0.005	67.85 ± 0.03
1-tdc:Men (1:2)	257.9 ± 2.9	872.06 ± 0.005	43.86 ± 0.01
1,2-dcd:Thy (1:2)	350.9 ± 5.5	952.33 ± 0.005	64.25 ± 0.06
1-Nap:Men (1:2)	200.0 ± 8.2	971.10 ± 0.005	120.90 ± 0.20
Atr:Thy (1:2)	1105.6 ± 13.2	1062.29 ± 0.005	86800[1]

The water contents of the DESs after preparation vary between approximately 200 to 1100 ppm, which are all low amounts of water, especially compared to the hydrophobic DESs based on quaternary ammonium salts described in Chapter 2. These had water contents between 920 to 8140 ppm.

Presumably, these low amounts of water in the hydrophobic DESs will only have small effects on the densities and viscosities. Of the 17 hydrophobic DESs tested, the densities of Dec:Atr (2:1), DodE:Atr (2:1), Thy:Cou (2:1), Thy:Cou (1:1), and Atr:Thy (2:1) are higher than that of water. The other 12 hydrophobic DESs have densities lower than water.

As mentioned before, a viscosity that is too high will lead to larger energy costs upon use in the industry. In Chapter 2 viscosities in the range of 173 to 783 $\mathrm{mPa \cdot s}$ were reported, while Ribeiro *et al.*[79] presented viscosities in the range of 10 to 220 $\mathrm{mPa \cdot s}$.[79,95] The 17 hydrophobic DESs presented in this chapter have viscosities ranging from 20 to 86800 $\mathrm{mPa \cdot s}$. Preferably, the viscosity should be as low as possible and comparable to water (1 $\mathrm{mPa \cdot s}$). Still, viscosities up to 100 $\mathrm{mPa \cdot s}$ are acceptable for industrial applications. From Table 3.2 it follows that the following DESs satisfy this criterion: DecA:Men (1:1), DecA:Men (1:2), Men:Lid (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2), 1-tdc:Men (1:2) and 1,2-dcd:Thy (1:2).

3.3.2 TGA

It is useful to quantify the temperature over which a DES can be used without solidification or degradation. Measuring melting temperatures for DESs is challenging since instead of a melting point a glass-transition temperature is often found.[58]

Hence, thermograms were measured to determine the degradation temperatures of the hydrophobic DESs. They represent the weight loss of a DES as a function of temperature. Thermograms selected with the criterion of a DES viscosity lower than 100 $\mathrm{mPa \cdot s}$ are presented in Figure 3.1 and Figure 3.2.

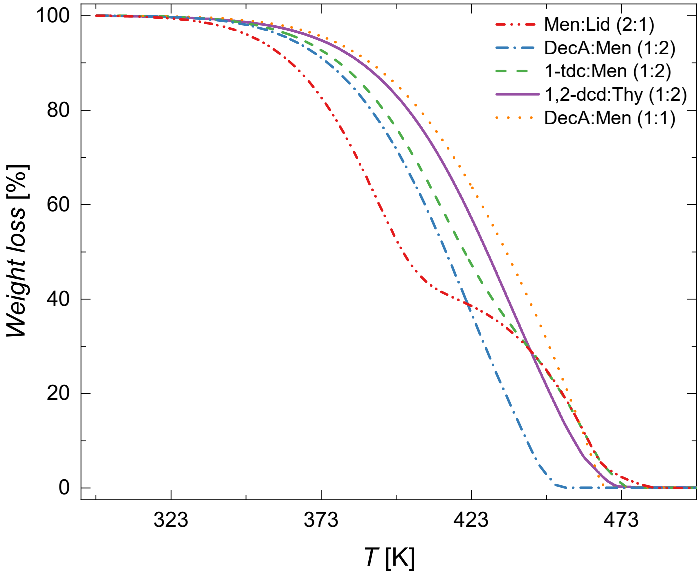


Figure 3.1: Thermograms of the DESs Men:Lid (2:1), DecA:Men (1:2), 1-tdc:Men (1:2), 1,2-dcd:Thy (1:2) and DecA:Men (1:1). The x-axis shows an increase in temperature [K], while the y-axis shows the loss in weight [%].

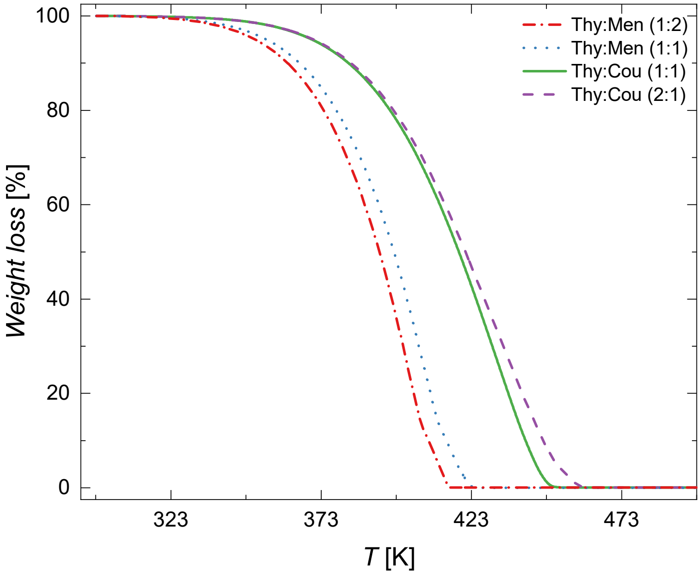


Figure 3.2: Thermograms of the DESs Thy:Men (1:2), Thy:Men (1:1), Thy:Cou (1:1), Thy:Cou (2:1) The x-axis shows an increase in temperature [K], while the y-axis shows the loss in weight [%].

The thermograms of the selected hydrophobic DESs all show a single-step decay of weight loss, except for Men:Lid (2:1). For this DES also a second plateau is observed. Most likely this second plateau is caused by significantly different degradation temperatures of the two components that form the DES. From Figure 3.1 it can be seen that the difference between the hydrophobic DESs DecA:Men (1:2) and DecA:Men (1:1) is large. Despite the fact that the same components are used for these two hydrophobic DESs, the thermogram for DecA:Men (1:1) has a much more delayed decay in weight loss than DecA:Men (1:2), which is quite remarkable. It is anticipated that this effect is due to a combination of a higher volatility of Men and a more preferred liquid structure in a DecA + Men mixture at the 1:1 ratio. For the hydrophobic DESs Thy:Men (1:1) and Thy:Men (1:2) and for Thy:Cou (1:1) and Thy:Cou (2:1) the differences in thermograms are only small.

Table 3.4: Degradation temperatures of the newly developed hydrophobic DESs.

DES	T_{deg} [K]
DecA:Lid (2:1)	443.1 ± 2.6
DecA:Atr (2:1)	444.8 ± 4.5
DecA:Men (1:1)	410.2 ± 2.0
DecA:Men (1:2)	382.9 ± 1.7
DodE:Lid (2:1)	459.8 ± 4.1
DodE:Atr (2:1)	477.0 ± 3.7
Men:Lid (2:1)	363.6 ± 0.4
Thy:Lid (2:1)	412.9 ± 4.5
Thy:Cou (2:1)	390.8 ± 2.9
Thy:Men (1:1)	381.9 ± 4.9
Thy:Lid (1:1)	424.4 ± 4.9
Thy:Cou (1:1)	392.9 ± 2.1
Thy:Men (1:2)	378.7 ± 3.8
1-tdc:Men (1:2)	386.3 ± 8.4
1,2-dcd:Thy (1:2)	395.7 ± 5.0
1-Nap:Men (1:2)	388.5 ± 6.9
Atr:Thy (1:2)	429.6 ± 2.1

Table 3.4 gives an overview of the degradation temperatures (T_{deg}) from the thermograms of the hydrophobic DESs. The results show that most of the T_{deg} values are lower than those of comparable ILs, which typically have a T_{deg} of 473 K and higher.[104,105] Moreover, in comparison with previously reported hydrophobic DESs based on decanoic acid and quaternary ammonium salts the T_{deg} values are lower.[95] It is assumed that these lower T_{deg} values do not present degradation, but reflect sublimation/evaporation of the components of the DESs. Components such as menthol, thymol, and coumarin have a high odor and it is known that they have the ability to sublimate.

Men:Lid (2:1) has a rather low T_{deg} of 363.6 K, although it should be mentioned that this temperature is based only on the first decay and not on the second one. All hydrophobic DESs based on thymol, menthol and coumarin have a melting point lower than 429.6 K. The combination of these 3 components have degradation temperatures between 378.7 K and 390.8 K. Thus, it can be observed that the combinations of the three most volatile components, thymol, menthol and coumarin, give lower T_{deg} than one of these components is mixed with a less volatile component such as decanoic acid, dodecanoic acid, lidocaine or atropine, ranging from 443.1 K to 477.0 K.

These results show that the degradation temperature and volatility highly depend on the components that are chosen. This is an important aspect one should account for when designing a DES for a certain application and holds for both hydrophilic and hydrophobic DESs. For aprotic ionic liquids it is generally known that they all have a moderate to high degradation temperature and a low volatility, less dependent on the types of components and composition.[104,105] For DESs, both the volatility as well as the degradation temperature should be properly investigated to quantify the boundary conditions when applying such solvents.

NMR on the DESs

NMR analysis was performed on the developed hydrophobic DESs. An example of an analyzed ^{1}H and ^{13}C NMR is shown in Figure 3.3 and Figure 3.4 for Thy:Cou in a theoretical 2:1 molar ratio. ^{1}H NMR was used to verify the experimental molar ratio of the DESs and to check whether reactions occur between the components. The ratio of the DES was determined by taking a specific peak of Thy and Cou and divide the integrals of these peaks. The peak of Thy at 3.25 ppm, labeled with number 19, has integral 2.00, while at 6.4 ppm, labeled with number 4 the peak of Cou has an integral of 1.00. Thus, the molar ratio of the Thy:Cou DES is indeed 2:1. Similar calculations were performed for the components of the other DESs and it is shown that they are all in the expected theoretical molar ratio, which is also an indication that no reaction occurred between the components.

^{13}C NMR was also performed to investigate whether the two components of the DES reacted with each other, which would lead to extra peaks in the NMR spectrum. As can be seen in Figure 3.4 for the DES Thy:Cou (2:1), the peaks attributed to the original components are clearly identified and no further additional peaks were found. Similar analyses performed in all the other DESs showed that the calculations of the experimental molar ratios match the theoretical expectations which confirmed that no reactions took place between the components of the DES.

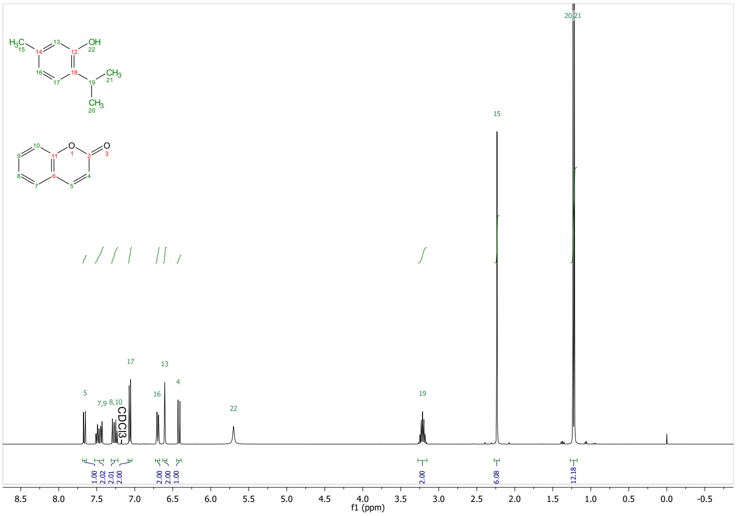


Figure 3.3: ^{1}H NMR of the DES Thy:Cou in a 2:1 molar ratio.

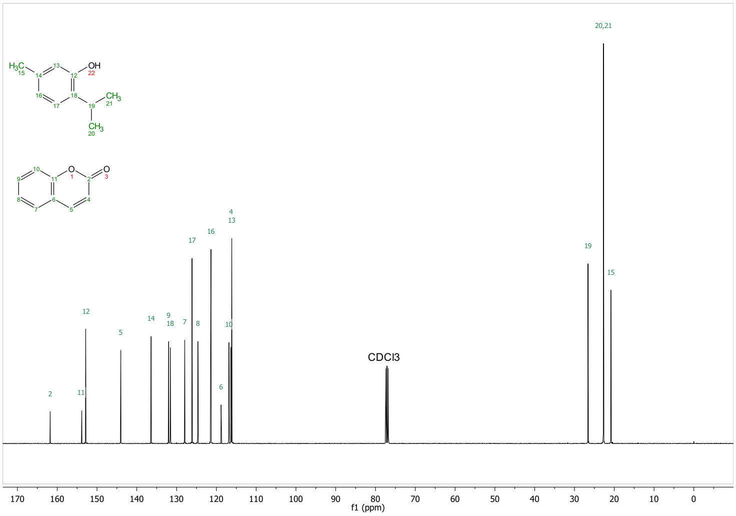


Figure 3.4: ^{13}C NMR of the DES Thy:Cou in a 2:1 molar ratio.

3.3.3 Density and viscosity after mixing with water

The developed hydrophobic DESs are interesting solvents for the removal or extraction of components from water, so it is useful to investigate how their properties change after mixing with water. Ideally, a fully separated system should be achieved with a pure DES phase in contact with a pure water phase, separated by a sharp interface. First, the water contents, densities and viscosities of the DESs after mixing with water are investigated. For the hydrophobic DESs composed of DodE:Lid (2:1) and DodE:Atr (2:1), no proper phase separation could be achieved after mixing the DESs with water, which is probably due to a combination of the density that is too close to that of water, a relatively high viscosity of the DES and a DES that is less hydrophobic. The results for the other hydrophobic DESs are depicted in Table 3.5. Since there is a finite solubility in water, the water contents of all DESs increase after mixing with water. Typically, DESs have a low to moderate water content after mixing with water, which varies from 1.64 to 5.14 wt%. The DES composed of 1-Nap:Men (1:2) has a rather low water content, of only 0.13 wt%. Two of the developed DESs have a high water content. DecA:Lid (2:1) has a water content of 20.6 wt%, while this is 33.9 wt% for DecA:Atr (2:1). It is hypothesized that this is attributed to the their less hydrophobicity and the fact that they easily form complexes with water.

The densities change slightly due to the uptake of water. The largest changes occur for DecA:Lid (2:1) and 1-Nap:Men (1:2). When these hydrophobic DESs are used in combination with water, complete phase separation is a necessity. In theory, phase separation gets more difficult (slower) when the density of the hydrophobic DES is closer to the density of water. The densities of DecA:Lid (2:1), DecA:Atr (2:1), Thy:Lid (2:1) and Thy:Lid (1:1) are very close to the density of water, which can delay phase separation and enhance emulsification. Preferably, the density between the DES and water is as large as possible, at least $50\,\mathrm{kg \cdot m^{-3}}$ and larger, such as for the DESs DecA:Men (1:1), DecA:Men (1:2), Men:Lid (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2) and 1-tdc:Men (1:2).

The addition of water to a hydrophobic DES normally leads to a decrease in viscosity, due to a small amount of water uptake combined with the fact that the viscosity of pure water is smaller. For most of the hydrophobic DESs tested here this applies. A small increase in viscosity is however observed for the DES DecA:Men (1:1). A thorough explanation for this behavior lacks, but one of the possibilities is that water is to some degree emulsified. For most DESs there is only a tiny decrease of the viscosity. Apparently, the increase of water content from ppm levels to approximately 1.64 to 5.14 wt% induces only minor changes. For example, DecA:Lid (2:1) has only a minor change in viscosity, while the increase in water content is large. The large decrease in viscosity for DecA:Atr (2:1) however does correspond to the increase of its water content. Moreover, the Atr:Thy (1:2) DES has a considerable decrease in the viscosity when water is added. To summarize, the DESs that satisfy the viscosity of 100 $\mathrm{mPa \cdot s}$ or lower after mixing with water are: Deca:Atr (2:1), DecA:Men (1:1), DecA:Men (1:2), Men:Lid (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2), 1-tdc:Men (1:2), 1,2-dcd:Thy (1:2), 1-Nap:Men (1:2) and Atr:Thy (1:2).

Table 3.5: Water contents, densities and viscosities of the hydrophobic DESs after mixing with water. The water contents of the water saturated DES were measured at room temperature (295 ± 1 K), while the densities and viscosities were measured at 298 K. For the water contents three or four consecutive measurements were performed, while for the densities and viscosites duplicates were measured from the same batch.

DES	Water content [wt%]	ρ [$\mathrm{kg \cdot m^{-3}}$]	η [$\mathrm{mPa \cdot s}$]
DecA:Lid (2:1)	20.63 ± 0.5	983.48 ± 0.165	141.6 ± 0.00
DecA:Atr (2:1)	33.86 ± 0.64	1025.47 ± 0.005	80.59 ± 1.69
DecA:Men (1:1)	2.10 ± 0.01	902.94 ± 0.005	20.47 ± 0.00
DecA:Men (1:2)	2.07 ± 0.01	902.34 ± 0.010	26.24 ± 0.04
Men:Lid (2:1)	2.41 ± 0.02	942.19 ± 0.00	59.00 ± 0.00
Thy:Lid (2:1)	1.64 ± 0.01	990.85 ± 0.005	100.20 ± 0.00
Thy:Cou (2:1)	2.48 ± 0.01	1050.0 ± 0.005	26.78 ± 0.01
Thy:Men (1:1)	1.81 ± 0.01	938.12 ± 0.010	42.01 ± 0.02
Thy:Lid (1:1)	1.77 ± 0.03	994.37 ± 0.005	149.80 ± 0.70
Thy:Cou (1:1)	2.54 ± 0.02	1090.24 ± 0.005	25.82 ± 0.01
Thy:Men (1:2)	1.69 ± 0.01	925.56 ± 0.00	52.17 ± 0.02
1-tdc:Men (1:2)	1.73 ± 0.01	874.22 ± 0.00	36.63 ± 0.01
1,2-dcd:Thy (1:2)	5.14 ± 0.02	956.31 ± 0.005	42.57 ± 0.02
1-Nap:Men (1:2)	0.13 ± 0.01	981.94 ± 0.005	74.43 ± 0.13
Atr:Thy (1:2)	3.00 ± 0.05	1061.02 ± 0.110	9255.5 ± 264.5

3.3.4 NMR after mixing with water

NMR analysis is also performed on the hydrophobic DESs after mixing with H_2O. For the DES Dode:Lid (2:1) and DodE:Atr (2:1) no suitable NMR analysis after mixing with water could be achieved due to difficulties with separating the two phases. As an example, for the DES composed of Thy and Cou the integrals of the peaks at 3.25 and 6.4 ppm give a molar ratio of 2:1 Thy:Cou, showing that the ratio of the DES is still the same. Moreover, all the other integrals are also in the expected ratio. A small peak around 1.8 ppm is present, which is not related to the pure DES components, hence it could be attributed to a small contamination, in this case by water, that is present either in the DES phase or the solvent $CDCl_3$.

In the ^{13}C NMR no extra peaks were observed, a sign that no reaction occurred between the two components of the DESs. All other NMRs of the DESs after mixing with water were analyzed in the same manner and showed molar ratios as expected. Thus, no reactions occurred between the components.

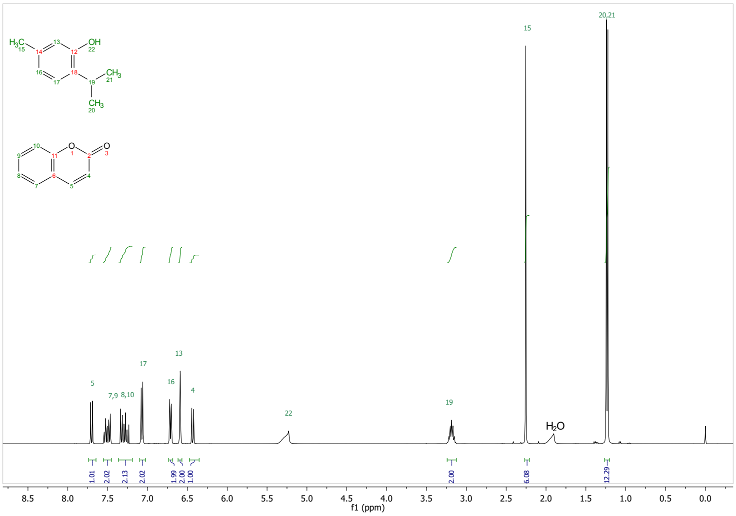


Figure 3.5: ^{1}H NMR of the DES Thy:Cou in a 2:1 molar ratio after mixing with H_2O.

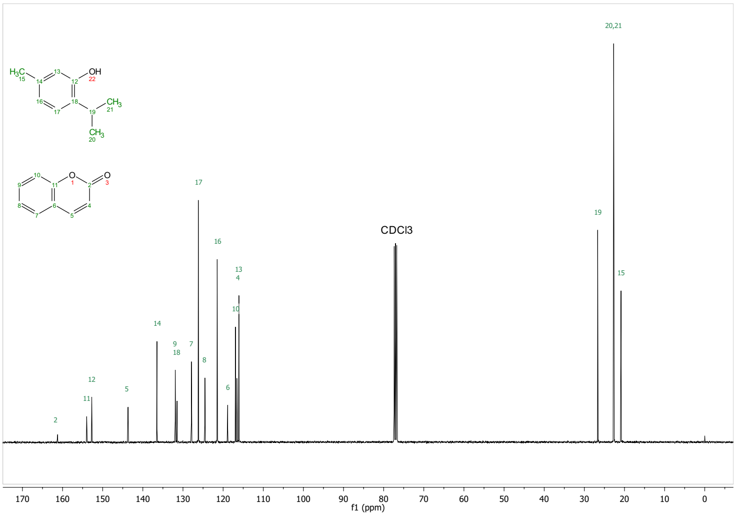


Figure 3.6: ^{13}C NMR of the DES Thy:Cou in a 2:1 molar ratio after mixing with H_2O.

3.3.5 pH of the water phase

When applying hydrophobic DESs for extraction purposes it is useful to verify whether the pH of the water phase upon mixing of the two phases is affected, since the change of pH indicates whether there is DES transfer to the water phase. A pH change can have a negative result on an extraction and if microorganisms are present in the water phase, it can even lead to their destruction. Furthermore, acidification or basification of water can have an undesirable effect on equipment. Thus, as a boundary condition the pH of the water phase after mixing with the hydrophobic DES should be between 6 and 8. From Table 3.6 it can be observed that eight hydrophobic DESs satisfy this criterion, namely DecA:Lid (2:1), DecA:Atr (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2), 1-tdc:Men (1:2), Atr:Thy (1:2). Surprisingly, DecA:Lid (2:1) has a neutral pH, while all water phases mixed with a DES composed of decanoic acid are acidic and all water phases mixed with a DES containing lidocaine become basic. Most likely the acidic and basic effect cancel each other out. The same also applies for DecA:Atr (2:1), where decanoic acid contains a carboxylic group and atropine contains an amine group. Moreover, it is remarkable that Atr:Thy (1:2) has a pH of 7.53. Atropine contains an amine group, while thymol has no groups that should induce a pH change so upon transfer of the components to the water phase it is expected they induce a pH > 7. Finally, it is peculiar that the pH of the water phase after contact with 1,2-dcd:Thy (1:2) is 4.64. Both components of these DES are alcohols, so the pH is expected to be close to 7 upon transfer to the water phase.

Table 3.6: pH of the water phases after mixing for 2 h with the hydrophobic DES.

DES	pH of the water phase
DecA:Lid (2:1)	6.96
DecA:Atr (2:1)	6.54
DecA:Men (1:1)	4.16
DecA:Men (1:2)	4.29
Men:Lid (2:1)	10.04
Thy:Lid (2:1)	9.15
Thy:Cou (2:1)	7.64
Thy:Men (1:1)	7.24
Thy:Lid (1:1)	9.29
Thy:Cou (1:1)	6.97
Thy:Men (1:2)	7.34
1-tdc:Men (1:2)	7.14
1,2-dcd:Thy (1:2)	4.64
1-Nap:Men (1:2)	5.95
Atr:Thy (1:2)	7.53

3.3.6 Total organic carbon content in the water phase

The total organic carbon (TOC) content was measured to quantify the amount of dissolved organic molecules in the water phase (Table 3.7). The TOC value of DecA:Lid (2:1) is considerably higher than the amounts measured previously. This can be explained by the difficult sampling of the water phase after centrifugation. All DESs prepared with atropine led to high TOCs in the coexisting water phase. The water phases in contact with hydrophobic DESs prepared with menthol had TOC values lower than 0.1 wt%, except for Men:Lid (2:1). It is hypothesized that this is caused by a complexation of menthol with lidocaine, leading to a complex that becomes slightly more hydrophilic in comparison with its pure component. Remarkably, also the DESs composed of thymol and coumarin have slightly higher TOC values. Overall, it can be concluded that the amount of organics that transfer to the water phase is rather low in comparison to the previously reported hydrophobic DESs in Chapter 2.

The amount of the organic phase that transfers to the water phase should be as low as possible. The field of ILs shows different ranges of transfer of the organic phase to the water phase. Parmentier et al.[10] showed that the water phase (0.05 M NaCl) contained approximately $31.5\,\mathrm{mg}\cdot\mathrm{L}^{-1}$ of the IL [P_{8888}][oleate] and values lower than 25 ppm for the tetraalkylammonium oleate and linoleate based ionic liquids in the water phase. In mole fractions this gives 7.41×10^{-7} ([P_{8888}][oleate]) and 6.02×10^{-7} ([N_{8888}][oleate]).[10,106] Freire et al.[107] showed that for the IL [C_4mim][$C(CN_3)$] a mole fraction of 5.62×10^{-3} is present in the water phase, while for fluorinated ILs these mole fractions vary between 1.01×10^{-3} ([C_4mim][PF_6]) to 3.54×10^{-4} for ([C_6mim][PF_6]).[107] In comparison, for the DES Thy:Cou (1:1) the mole fraction of total organic carbon that is dissolved in the water phase is 1.43×10^{-4} , while this is 2.80×10^{-5} for 1-tdc:Men (1:2). Thus, the amount of the newly developed hydrophobic DES that transfers to the water phase is comparable to what was found for fluorinated ILs, except for DecA:Lid (2:1), DecA:Atr (2:1), Men:Lid (2:1), and Atr:Thy (1:2).

Table 3.7: TOC values in the water phases measured with a Shimadzu TOC-L CPH/CPN (see also the experimental section).

DES	TOC value [ppm]
DecA:Lid (2:1)	58489
DecA:Atr (2:1)	6475
DecA:Men (1:1)	276
DecA:Men (1:2)	390
Men:Lid (2:1)	2108
Thy:Lid (2:1)	777
Thy:Cou (2:1)	1162
Thy:Men (1:1)	583
Thy:Lid (1:1)	1175
Thy:Cou (1:1)	1596
Thy:Men (1:2)	474
1-tdc:Men (1:2)	273
1,2-dcd:Thy (1:2)	898
1-Nap:Men (1:2)	795
Atr:Thy (1:2)	4917

3.3.7 NMR analysis of the water phases

Since the TOC only gives information regarding the amount of total organic carbon in the water phase, NMR analysis was performed to investigate the relative amount of the components of the hydrophobic DES that transfer to the water phase. Hence, ^{1}H NMR spectra were taken of the water phase after mixing with DES, as discussed previously.

An example is given in Figure 3.7 for the water phase after mixing it with the hydrophobic DES Thy:Men (1:1). The specific peaks for Thy were located between 6.6 and 7.2 ppm, while Men had peaks just before 2.0 ppm and between 3.0 and 3.5 ppm. For example, the integral of the peak of Thy at 7.2 ppm can be divided by the integral of the peak of Men at 3.4 ppm. This gives a molar ratio of Thy:Men in the water phase of 3.0:1.0. The spectrum also shows that within the same molecule there is a difference in the estimated integrals, as is shown for Thy between 6.6 and 7.2 ppm. This could be caused by impurities present in the original components of the DESs that at these low concentrations may still be visible.

Despite the fact that this method gives no precise ratios of which component transfers to the water phase, it gives a good indication of the different molar ratios of the components in the water phase. The estimated ratios in water are given in Table 3.8. It is clear that the portioning of the two DES components over the DES-rich and water-rich phases is rather asymmetric and random. Further detailed analyses or interpretation of the current data is not viable, neither within the scope of the current work, but certainly worth exploring in future works.

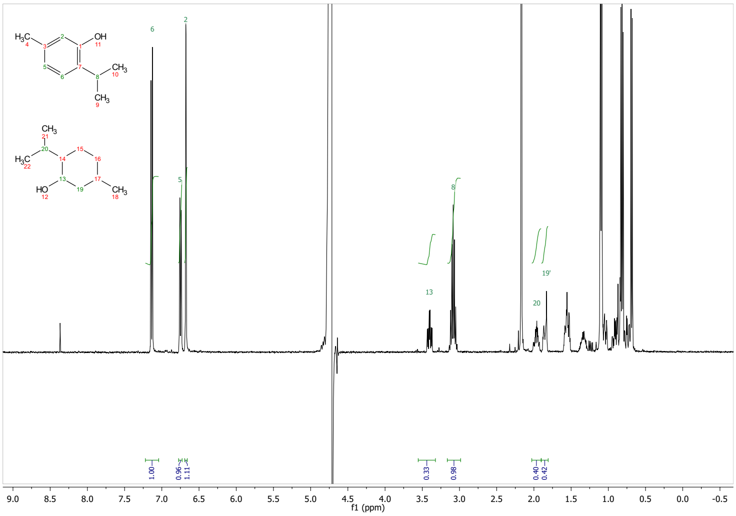


Figure 3.7: ^{1}H NMR of the water phase after mixing with Thy:Men (1:1) with a suppression of the water peak.

Table 3.8: Molar ratio between the components that transfer to the water phase determined via ^{1}H NMR of the water phase.

DES	Molar ratios of DES in H_2O [ppm]
Men:Lid (2:1)	Men:Lid - 1.0:7.1
Thy:Lid (2:1)	Thy:Lid - 1.6:1.0
Thy:Cou (2:1)	Thy:Cou - 1.0:1.3
Thy:Men (1:1)	Thy:Men - 3.0:1.0
Thy:Lid (1:1)	Thy:Lid - 1.0:6.0
Thy:Cou (1:1)	Thy:Cou - 1.0:2.9
Thy:Men (1:2)	Thy:Men - 1.6:1.0
1-tdc:Men (1:2)	1-tdc:Men - 1.0:3.2
1,2-dcd:Thy (1:2)	1,2-dcd:Men - 1.0:2.9
1-Nap:Men (1:2)	1-Nap:Men - 5.3:1.0
Atr:Thy (1:2)	Atr:Thy - 24.2:1.0

3.4 Application: extraction of riboflavin from water

To verify whether the selected hydrophobic DESs are capable of extracting compounds from water, the removal of rifoblavin (vitamin B2) from the aqueous solutions is investigated. Riboflavin was chosen because it is one of the most necessary vitamins for humans and challenging to extract from aqueous solutions. High performance liquid chromatography (HPLC) was used to measure the concentration of riboflavin before and after extraction. From the concentrations the distribution coefficient (K) can be calculated:

$$K = \frac{C_{\text{vitB2}}^{\text{ini}} - C_{\text{vitB2}}^{\text{fin}}}{C_{\text{vitB2}}^{\text{ini}}} \tag{3.1}$$

In Equation 3.1, $C_{\text{vitB2}}^{\text{ini}}$ is the initial concentration of the riboflavin in H_2O in wt% and $C_{\text{vitB2}}^{\text{fin}}$ is the final concentration of riboflavin in H_2O in wt% after mixing with the DES. This implies that complete extraction corresponds to K = 1 and no extraction implies K = 0. K values between 0.3 and 0.7 can be seen as moderate, while $>$ 0.7 can be seen as good K. The results are presented in Table 3.9.

Table 3.9: DES-water distribution coefficients (K) of riboflavin for H_2O for the different selected hydrophobic DESs.

DES	K [ppm]
DecA:Men (1:1)	0.21 ± 0.02
Thy:Lid (2:1)	0.32 ± 0.05
DecA:Lid (2:1)	0.81 ± 0.04
1-tdc:Men (1:2)	0.61 ± 0.01
Thy:Cou (2:1)	0.71 ± 0.01
Thy:Cou (1:1)	0.48 ± 0.01
Thy:Men (1:2)	0.54 ± 0.01
Thy:Men (1:1)	0.54 ± 0.01
DecA:N_{8888}-Br	0.19 ± 0.01

The results of the selected hydrophobic DESs as presented in Table 3.9 were compared with one of the first developed ones, the DES composed of decanoic acid and tetraoctylammonium bromide in a 2:1 molar ratio (see Chapter 2). This DES had a K of 0.19, while DecA:Men (1:1) extracted the lowest amount of the new hydrophobic DESs with approximately a K of 0.21. Thus, all new hydrophobic DESs had a higher distribution coefficient than the one composed of decanoic acid and tetraoctylammonium bromide that in Chapter 2 was used for the extraction of volatile fatty acids. The highest extraction efficiency was achieved with the hydrophobic DES DecA:Lid (2:1), a DES which is also very capable of extracting metal ions from water (see Chapter 5). Varying the ratios of the DES had no influence on the distribution coefficients for the DES consisting of thymol and menthol, while a difference in distribution coefficient of approximately 0.23 was observed for the DES that was prepared from thymol and coumarin. In general, all newly developed hydrophobic DESs showed moderate to good distribution coefficients in comparison to the DES as presented in Chapter 2. A precise reason for this is not clear, but it is hypothesized that different factors play a role in this, e.g. pH change of the water phase due to certain solubilities of the pure components, the hydrophobicity of the DES and interaction between the DES and riboflavin.

3.5 Conclusions and outlook

In this work a series of new, sustainable, hydrophobic DESs was reported. From 507 combinations of two solid components, 17 became a liquid at room temperature, which were further assessed for their sustainability via four criteria. These criteria are based on the use of the hydrophobic DESs as extractants and include a viscosity below 100 mPa·s, a density that should be rather different than the density of the water phase, a limited pH change of the water phase upon mixing with water and a low amount of DES that transfers to the water phase.

More than 10 DESs follow the viscosity criterion below 100 mPa · s. Regarding the density, the criterion was set at a density difference between the DES and water as large as possible ($\rho \geq 50\,\mathrm{kg \cdot m^{-3}}$). The hydrophobic DESs Deca:Men (1:1), DecA:Men (1:2), Men:Lid (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2) and 1-tdc:Men (1:2) satisfy this criterion.

Furthermore, the criterion of a limited pH change (between 6 and 8) of the water phase coexisting with the DES showed that the hydrophobic DESs DecA:Lid (2:1), DecA:Atr (2:1), Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2), 1-tdc:Men (1:2) and Atr:Thy (1:2) have a negligible pH change. The amount of organics that transfers to the water phase was comparable for all developed hydrophobic DESs, except for DecA:Lid (2:1), DecA:Atr (2:1), and Atr:Thy (1:2), which had considerably higher TOC values.

In general, the newly developed DESs Thy:Cou (2:1), Thy:Men (1:1), Thy:Cou (1:1), Thy:Men (1:2) and 1-tdc:Men (1:2) satisfied all four criteria. Therefore, these hydrophobic DESs may be considered as relatively sustainable, hydrophobic designer solvents. These DESs were used for the removal of riboflavin from an aqueous environment. All new hydrophobic DESs showed moderate to high extraction yields.

In the future, these hydrophobic DESs should be further investigated to fully understand their solid-liquid equilibria and their liquid-gas equilibria. These fundamentals will give us a deeper understanding of these complex eutectic mixtures and enable to quantify the range of molar ratios where the mixtures are a liquid. Moreover, their biodegradability and toxicity should be addressed.

3.6 Appendix: NMRs of the water phases after mixing with the hydrophobic DESs

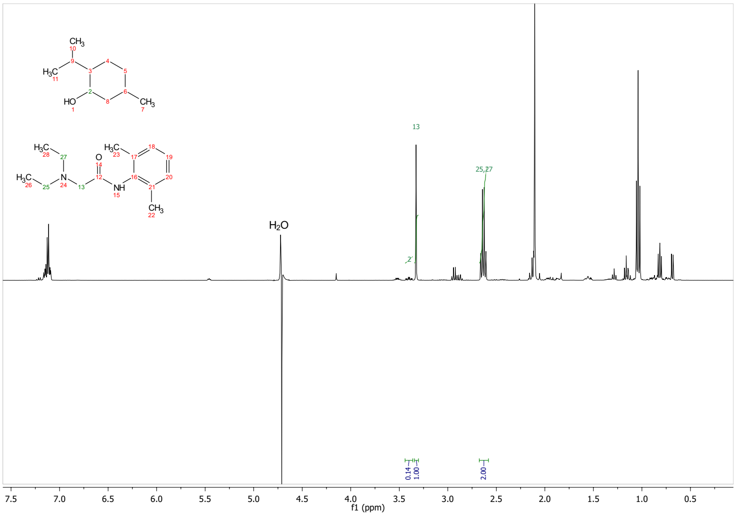


Figure 3.8: ^{1}H NMR of the water phase after mixing with Men:Lid (2:1) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

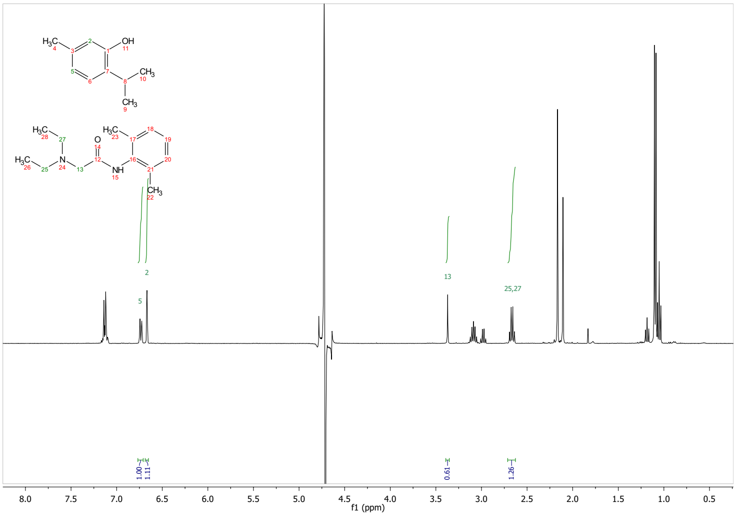


Figure 3.9: ^{1}H NMR of the water phase after mixing with Thy:Lid (2:1) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

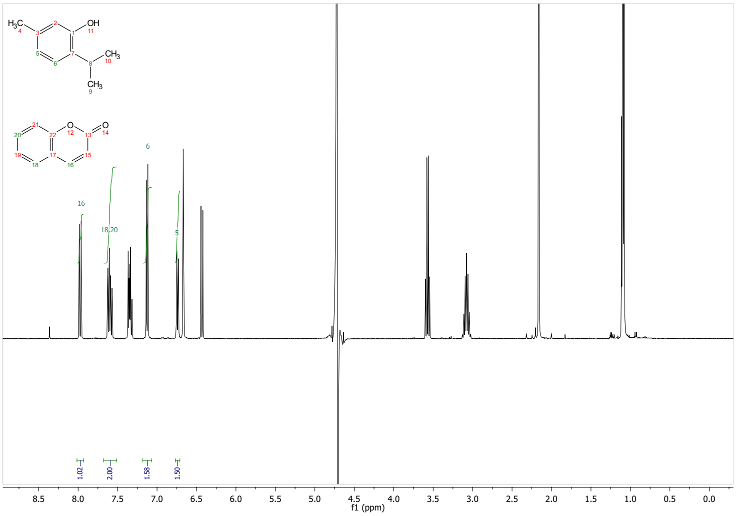


Figure 3.10: ^{1}H NMR of the water phase after mixing with Thy:Cou (2:1) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

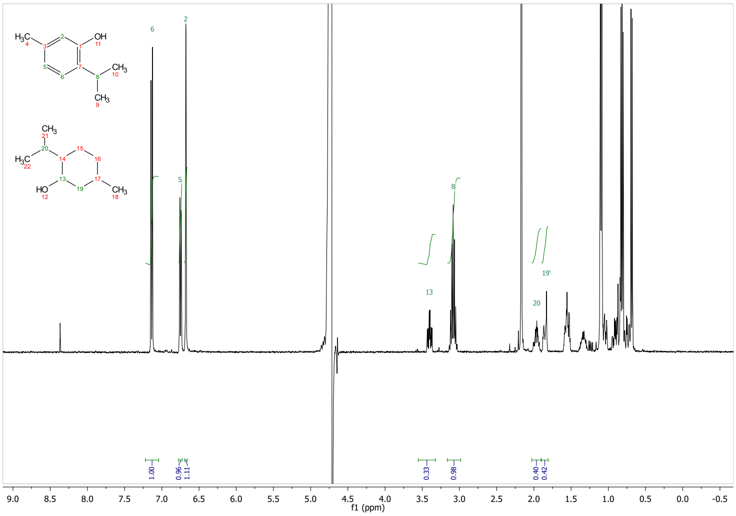


Figure 3.11: ^{1}H NMR of the water phase after mixing with Thy:Men (1:1) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

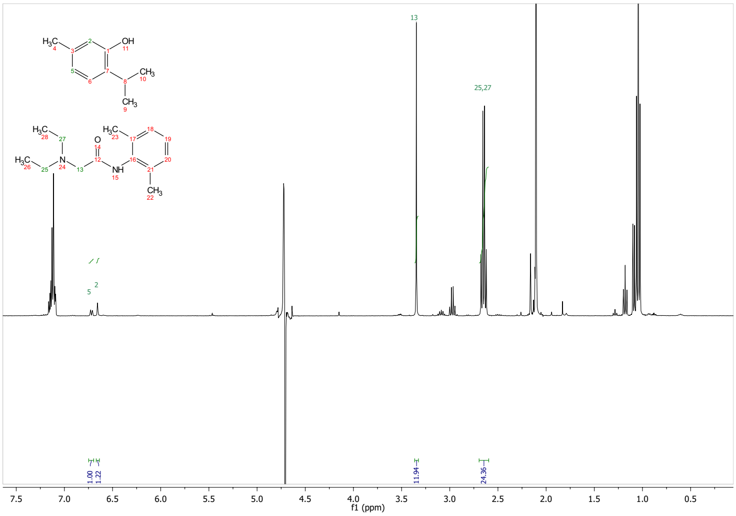


Figure 3.12: ^{1}H NMR of the water phase after mixing with Thy:Lid (1:1) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

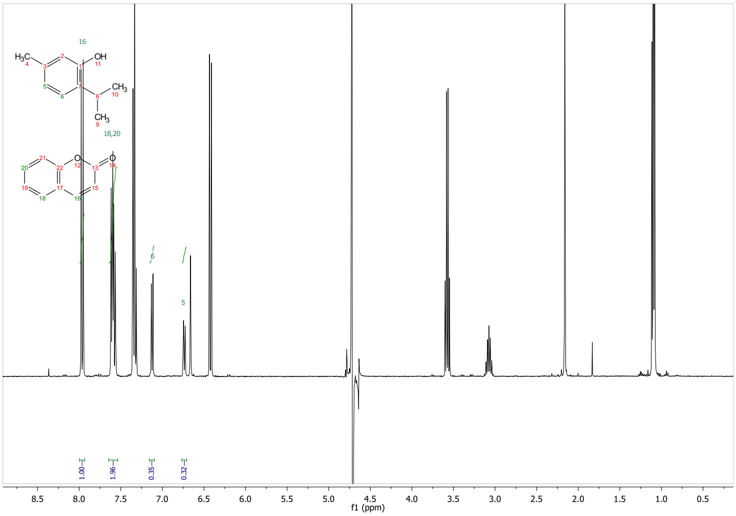


Figure 3.13: ^{1}H NMR of the water phase after mixing with Thy:Cou (1:1) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

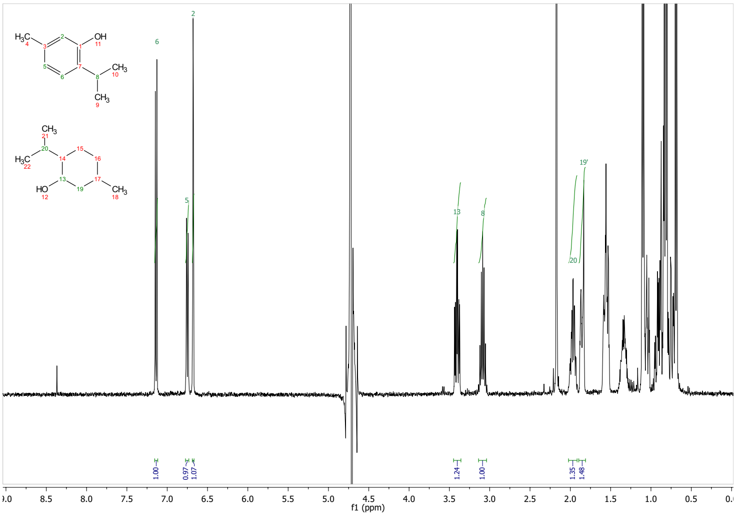


Figure 3.14: ^{1}H NMR of the water phase after mixing with Thy:Men (1:2) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

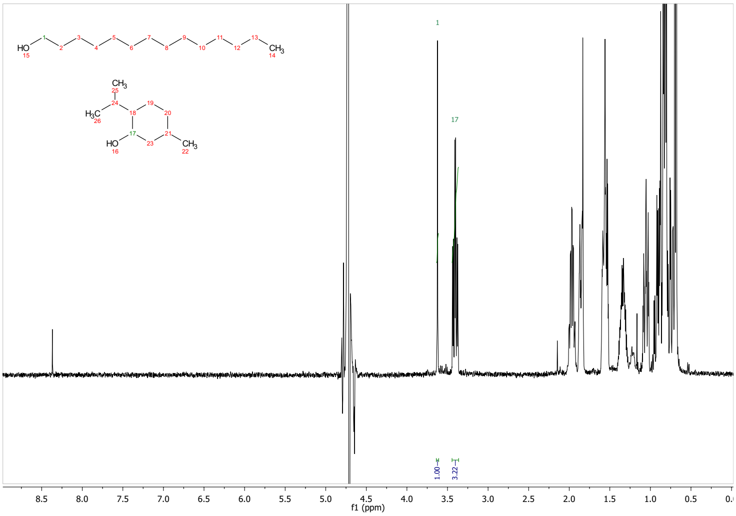


Figure 3.15: ^{1}H NMR of the water phase after mixing with 1-tdc:Men (1:2) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

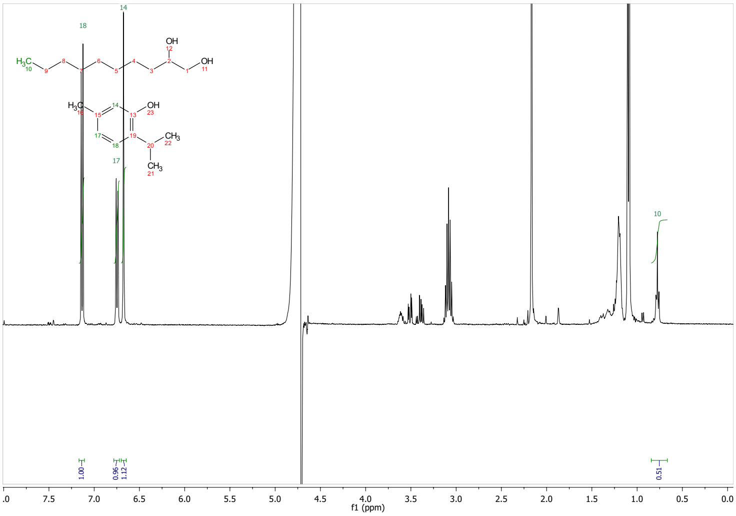


Figure 3.16: ^{1}H NMR of the water phase after mixing with 1,2-dcd:Thy (1:2) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

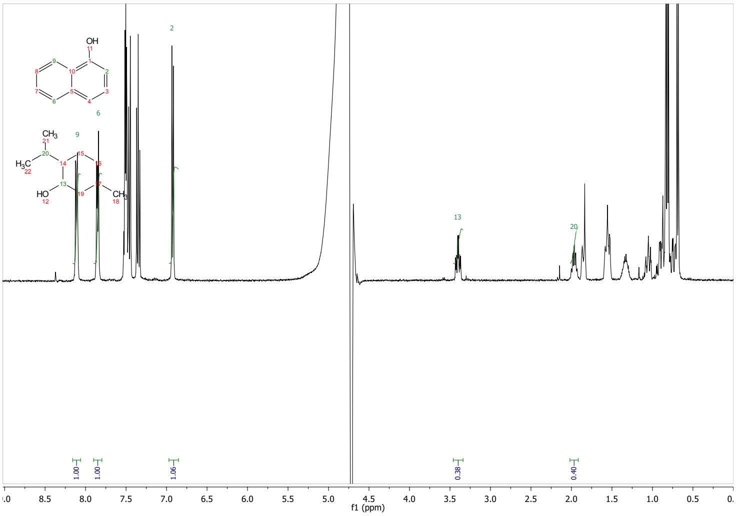


Figure 3.17: ^{1}H NMR of the water phase after mixing with 1-Nap:Men (1:2) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

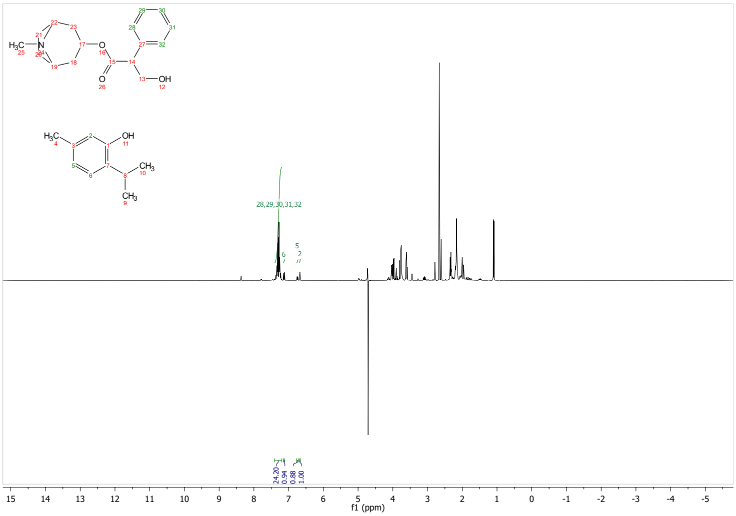


Figure 3.18: ^{1}H NMR of the water phase after mixing with Atr:Thy (1:2) with a suppression of the water peak, which is the broad peak around 4.75 ppm.

Chapter 4

The Solubility of CO_2 in Hydrophobic Deep Eutectic Solvents

Abstract

The aim of this chapter is to evaluate the solubility of CO_2 in hydrophobic deep eutectic solvents (DESs). Six decanoic based hydrophobic DESs are tested and compared to conventional solvents. The results show that hydrophobic DESs have CO_2 capture ability comparable to fluorinated ionic liquids. Theoretical modeling of the solubilities is performed with the PC-SAFT 'pseudo-pure' approach. Only liquid density data is needed to obtain the segment number, the temperature-independent segment diameter and the dispersion-energy diameter to model the CO_2 solubility in hydrophobic DESs. The results show that the solubilities of the hydrophobic DESs can be predicted with the PC-SAFT model with parameters only fitted to liquid densities.

This chapter is a modified version of:
Lawien F. Zubeir[1], Dannie J.G.P. van Osch[1], Marisa A.A. Rocha, Fawzi Banat, Maaike C. Kroon, Carbon Dioxide Solubilities in Decanoic Acid-Based Hydrophobic Deep Eutectic Solvents, *J. Chem. Eng. Data*, 2018, **63**, 913-919
and
Carin H.J.T. Dietz[1], Dannie J.G.P van Osch[1], Maaike C. Kroon, Gabriele Sadowski, Martin van Sint Annaland, Fausto Gallucci, Lawien F. Zubeir, Christoph Held, PC-SAFT modeling of CO_2 solubilities in hydrophobic deep eutectic solvents, *Fluid Phase Equib.*, 2017, **448**, 94-98
[1]**combined first authorship**

4.1 Introduction

Carbon dioxide (CO_2) is one of the greenhouse gases contributing to global warming. It is estimated that more than 60 % of the global warming is caused by the emission of CO_2. To avoid any further global warming, the capture of this greenhouse gas should be addressed.[108] The steps for the capture and storage of CO_2 that are already developed and are economically feasible are transportation, compression and storage. However, the main costs, approximately two-thirds, come from the capture stage. Especially the solvent regeneration has a major impact on the costs.[16]

Two methods used for the capture of CO_2 are chemical and physical absorption.[109] Chemical absorption is used at low CO_2 concentrations with alkanolamine solutions, but has major drawbacks. These include a large volume of absorber needed, high equipment corrosion rates and high energy consumption.[109] Physical absorption is used at higher CO_2 concentrations with solvents such a dimethylether, propylene glycol and methanol.[109] Disadvantages of physical absorption are low CO_2 absorption capability and low yields by the uptake of high amounts of hydrocarbons. Commercial processes based on physical absorption are the Selexol-, Rectisol-, Purisol-, Morphysorb-, and the Fluor-process.[109]

Recently, more innovative solvents have been tested for their ability to capture CO_2, i.e. ionic liquids (ILs). Due to their non-volatility and tunable physicochemical properties they have shown to be excellent solvents for CO_2 capture.[110] However, their synthesis and purification still makes them to expensive for use in the industry. ILs that show high solubility of CO_2 are $[C_4mim][TF_2N]$ and$[C_4mim][BF_4]$.[110]

More recently, CO_2 solubilities in hydrophilic DESs were presented in the literature. Hydrophilic DESs investigated for their CO_2 solubilities include urea:choline chloride (2:1),[111] ethylene glycol:choline chloride (2:1),[112] lactic acid:tetramethylammonium chloride (2:1),[32] lactic acid:tetraethylammonium chloride (2:1),[32] lactic acid:tetrabutylammonium chloride (2:1) and many more.[61,113] Despite that hydrophilic DESs were investigated in depth, none of them showed CO_2 solubilities comparable to ILs.

In this chapter solubilities of CO_2 in hydrophobic DESs are presented.

The hydrophobic DESs composed of decanoic acid in combination with tetrabutylammonium chloride ($N_{4444}-Cl$), methyltrioctylammonium chloride ($N_{8881}-Cl$), methyltrioctylammonium bromide ($N_{8881}-Br$), tetraoctylammonium chloride ($N_{8888}-Cl$), and tetraoctylammonium bromide ($N_{8888}-Br$) are investigated. The hydrogen bond donor (HBD) to hydrogen bond acceptor (HBA) ratio, the effect of the halide, and the effect of the quaternary ammonium salts on the CO_2 solubility are evaluated. Furthermore, the CO_2 solubilities in hydrophobic DESs are compared with ILs and conventional organic solvents.

This chapter also presents the Perturbed-Chain Statistical Associating Fluid Theory PC-SAFT ‘pseudo-pure’ component approach for predicting CO_2 solubilities in hydrophobic DESs. Due to the many combinations of hydrophobic DESs possible it would become time-consuming and costly to investigate all of them experimentally. Thus, it is of importance that a simple, robust model is developed that can predict solubilities of CO_2 in hydrophobic DESs. Recently, PC-SAFT was used for modelling CO_2 solubilities in hydrophilic DESs.[114] Two approaches were used, the ‘pseudo-pure’ component approach and the ‘individual-component approach’. For the ‘individual-component’ approach solubilities of the pure components in water are needed. Thus, it was chosen to use the ’pseudo-pure’ component approach.

4.2 Experimental section

4.2.1 Materials and preparation method

Materials

Table 4.1 gives an overview of the chemicals used throughout the investigation.

Table 4.1: CAS number, purity and supplier of the chemicals used in this investigation.

Component	CAS	Purity [%]	Supplier
Decanoic acid (2:1)	334-48-5	≥98	Sigma Aldrich
$N_{4444}-Cl$	1112-67-0	≥95	Merck
$N_{8881}-Br$	35675-80-0	≥97	Sigma Aldrich
$N_{8881}-Cl$	5137-55-3	≥97	Sigma Aldrich
$N_{8888}-Br$	14866-33-2	≥97	Sigma Aldrich
$N_{8888}-Cl$	3125-07-3	≥98	Sigma Aldrich
CO_2	124-38-9	≥99.995	Sigma Aldrich

Preparation of the DES

The DESs were prepared in a capped glass bottle. First, the quaternary ammonium salt (HBA) was added to the glass bottle, after which the decanoic acid (HBD) was added via a weighing boat. A Sartorius extended ED224S balance with 0.1 mg readability was used. The two solid components were thoroughly shaken with a VWR Analog Vortex Mixer for approximately 10 s to mix the two solids properly, after which they were heated at 308 K in a thermostatic oil bath to obtain a liquid phase. The temperature was controlled with an IKA ETS-D5 temperature controller with an uncertainty of ± 0.1 K. An IKA RCT basic was used for monitoring the stirring speed and temperature.

Karl-Fischer measurements

The water contents were measured via Karl-Fischer titration with a 795 volumetric KFT Tritrino from Metrohm.

Density measurements

An Anton Paar SVM 3000 Stabinger Viscometer was used for determining the density (ρ) at 298 K. The absolute uncertainty in the density is $0.5\,\mathrm{kg}\cdot\mathrm{m}^{-3}$, while the temperature uncertainty is ± 0.2 K.

Procedure for mixing the DES with water

10 grams of hydrophobic DES and 10 grams of milliQ H_2O were added to a 50 mL centrifuge tube (CELLSTAR®). The samples were mixed on an IKA KS 4000 I incubating shaker (500 RPM, RT) for 2 hours. After shaking, the samples were centrifuged for 10 minutes at 10000 RPM. The water phase was taken with a needled syringe, after which the pH was measured.

pH measurements

The pH measurements were performed with an inoLab pH 730.

Carbon dioxide solubility measurements

Carbon dioxide measurements were performed with a magnetic suspension balance (MSB, Rubotherm GmbH), which determined the bubble-point curves. It can be used within the temperature range of 273.15 to 423.15 K and pressures varying from ultrahigh vacuum to 15 MPa. The temperature was regulated with a Julabo FP50-ME that externally pumps silicon oil through the Rubotherm. The temperature is measured with a platinum resistance probe (Pt-100). For a more in depth explanation of the Rubotherm equipment we would like to redirect you to the literature.[32]

4.3 Modelling

PC-SAFT has been first introduced by Gross and Sadowski.[115,116] It is based on statistical thermodynamics from Barker and Henderson in 1967.[117,118] PC-SAFT is a perturbation theory, which accounts for association and dispersive forces. SAFT commonly calculates the residual Helmholtz energy based on the difference between the total molar Helmholtz energy and the Helmholtz energy of an ideal gas. In PC-SAFT the residual molar Helmholtz energy is calculated by the sum of hard-chain interactions, energy contribution due to dispersion forces and site-site specific bonding interactions. For more information regarding PC-SAFT, the corresponding formulas and the modeling of gas solubilities an interested reader is referred to some comprehensive literature.[115,116]

The pure component parameter estimation and the applied modeling strategy was inherited from Zubeir *et al.*[114] with the understanding that only the pseudo-pure modeling strategy is used in this work. This strategy is briefly summarized here. The estimated parameters are: the segment number ($m_{\text{seg,i}}$), the temperature-independent segment diameter (σ_{i}), the dispersion-energy parameter ($u_{\text{i}}/k_{\text{B}}$), the association-energy parameter ($\epsilon^{\text{AiBi}}/k_{\text{B}}$) and the effective volume of an association site (κ^{AiBi}) . As these parameters were not available in literature, they were estimated in this work by fitting to experimental liquid density data from literature.[95] In contrast, the association-energy parameter ($\epsilon^{\text{AiBi}}/k_{\text{B}}$) and the effective volume of an association site (κ^{AiBi}) were not fitted to density data, as density data is inappropriate for fitting these association parameters. Thus, they were set to constant values according to suggestions from previous works.[32,119–121] For the formation of the DES, self-association via hydrogen bonding between the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) was considered. Thus, two association sites were accredited to the DES.

4.4 Results and Discussion

4.4.1 Influence of molar volume on CO_2 solubilities

Table 4.2: Molar mass [$g \cdot mol^{-1}$], density [$kg \cdot m^{-3}$] and molar volume [$cm^3 \cdot mol^{-1}$] of the reported hydrophobic DESs.

Component	M [$g \cdot mol^{-1}$]	ρ [$kg \cdot m^{-3}$]	V_m [$cm^3 \cdot mol^{-1}$]
DecA:$N_{4444}-Cl$ (2:1)	207.41	916.8	226.2
DecA:$N_{8881}-Br$ (2:1)	264.31	942.2	280.5
DecA:$N_{8881}-Cl$ (2:1)	249.49	896.4	278.3
DecA:$N_{8888}-Br$ (2:1)	297.04	929.8	319.5
DecA:$N_{8888}-Cl$ (2:1)	282.22	888.1	317.5
DecA:$N_{8888}-Cl$ (1.5:1)	304.23	888.9	342.6

Five different hydrophobic DESs, described in Table 4.2 with their molecular weight, densities and molar volumes, were investigated for their CO_2 solubility. Solubilities of CO_2 up to 2 MPa pressure were tested at three different temperatures, e.g. 298, 308 and 323 K. It was anticipated that the hydrophobic DESs physically absorb CO_2 such as for ILs.[122] The amount that can be solubilized depends on the free volume in the solvent, e.g. the molar volume. The higher the molar volume, the higher the amount of CO_2 that can be absorbed. Figure 4.1 shows that this assumption indeed applies for the decanoic acid based hydrophobic DESs since at a pressure of 2.0 MPa there is a gradually increase of the mole fraction of CO_2. A similar increase as is shown in Table 4.2.

Another factor investigated was the influence of the halide of the quaternary ammonium salt, –Br or –Cl, for N_{8888} and N_{8881}. Only minor differences in CO_2 solubilities were measured, which can be attributed to slight changes in their molar volumes. Changing the quaternary ammonium salt from the methyltrioctylammonium to tetraoctylammonium increased the solubility of CO_2, due to an increase of molar volume.

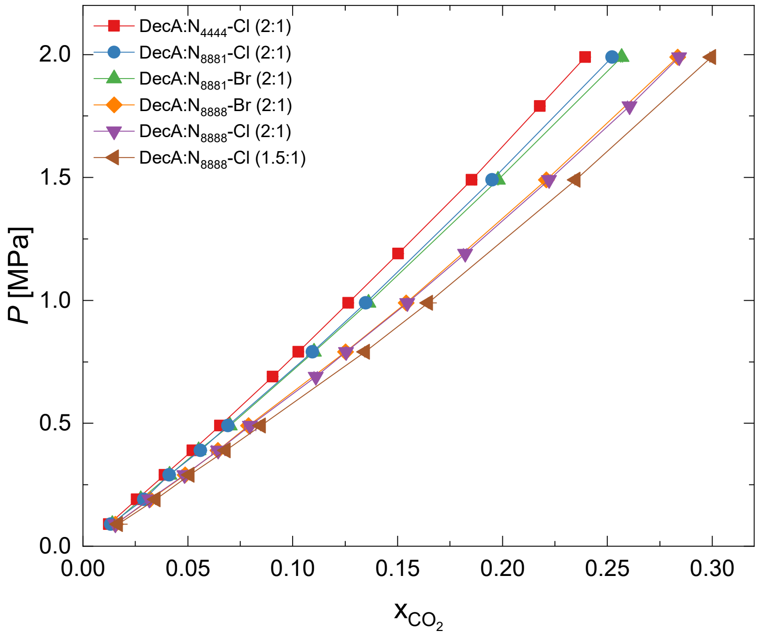


Figure 4.1: Solubility isotherms of CO_2 in the hydrophobic DESs as a function of pressure.

In the literature it was shown that changing the ratio between the hydrogen bond donor (HBD) and the hydrogen bond acceptor (HBA) induced a change in the solubility.[32] Thus, it was investigated what the lowest molar ratio of DecA:$N_{8888}-Cl$ was, where still a liquid was formed. It was found that this molar ratio was 1.5:1. As predicted, this hydrophobic DES has the highest solubility of CO_2 (Figure 4.1).

4.4.2 Influence of temperature on the CO_2 solubilities

Next to investigating the influence of changes in the DES structure, it was also decided to vary the temperature. Figure 4.2 shows the influence of temperature on the solubility of CO_2 in DecA:$N_{8888}-Cl$ (1.5:1). As expected, increasing the temperature lowers the solubility of CO_2. This can be explained by a decrease in the density, which leads to a lower molar volume.

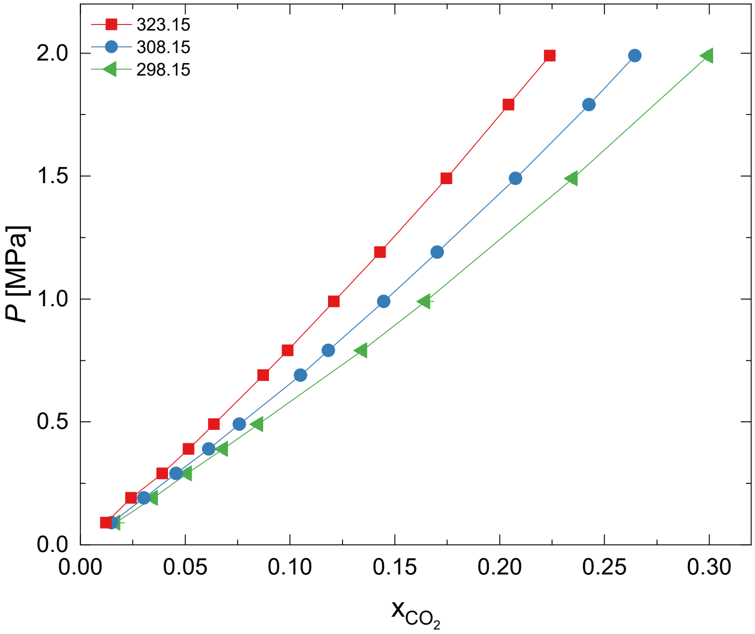
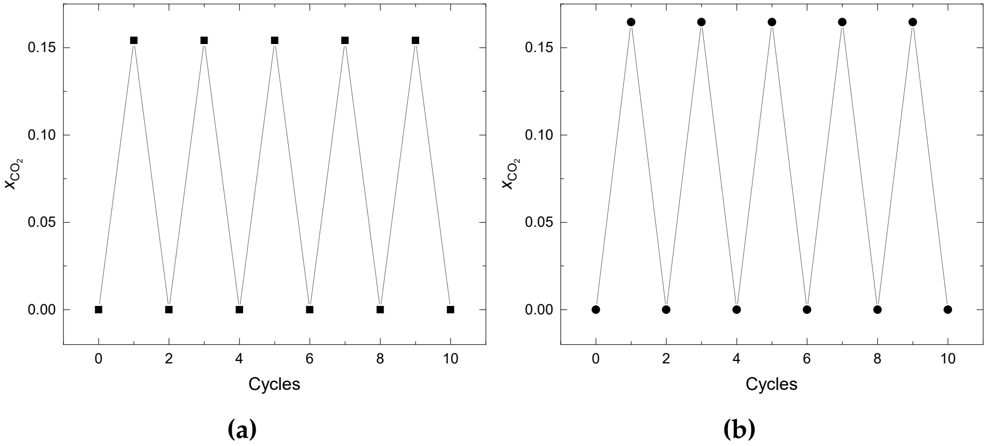


Figure 4.2: Solubility isotherms of CO_2 in the hydrophobic DESs as a function of temperature for the DES DecA:$N_{8888}-Cl$ (1.5:1).

4.4.3 Regeneration

An important aspect in case of physical absorption is the regeneration of the CO_2. At a temperature of 308 K and reduced pressure all the CO_2 could be regenerated without sample loss. (Figure 4.3).

^{13}C NMR was investigated before and after CO_2 absorption and regeneration to investigate whether CO_2 reacts with the hydrophobic DESs (Paragraph 4.6.1). No additional peaks appeared in the ^{13}C NMR spectrum after absorption and regeneration of the DESs. Thus, these two methods prove that the



(a) **(b)**

Figure 4.3: Cycles of CO_2 absorption for DecA:$N_{8888}-Br$ (2:1) (4.3a) and DecA:$N_{8888}-Br$ (1.5:1) (4.3b). Absorption is performed at 298.15 K and 1 MPa, while regeneration of the solvent was done at 308.15 K under vacuum.

hydrophobic DESs are stable under the experimental conditions and can be used for both the absorption and the regeneration of CO_2.

4.4.4 The Henry's law constants

Henry law's constant was determined from the solubility data, which gives more information regarding the solubility of a solute in a solvent. This constant only applies at low solubilities of CO_2 in the hydrophobic DESs. According to Henry's law the fraction of gas dissolved in the liquid phase is proportional to its fugacity in the gas phase as depicted in Equation 4.1:

$$H_{2,1}(T,P) = \lim_{x_2 \to 0} \frac{\hat{f}_2 \left(T_{\mathrm{eq}}, P_{\mathrm{eq}}, x_2\right)}{x_2} = \frac{\hat{\phi}_2 \left(T_{\mathrm{eq}}, P_{\mathrm{eq}}, x_2\right)}{x_2} \tag{4.1}$$

In this equation $H_{2,1}(T,P)$ is Henry's constant, x_2 is the mole fraction of CO_2 in the hydrophobic DES, $\hat{f}_2$ is the fugacity of the CO_2, $\hat{\phi}_2$ is the fugacity coefficient calculated with the Peng-Robinson equation of state and P_{eq} is the CO_2 pressure at phase equilibrium.[114] It was assumed that the fugacity of the hydrophobic DESs is negligible at the experimental conditions since their volatilities are low, which is also shown from the TGAs in paragraph 2.5.1. Thus, the fugacity of the DES+CO_2 equals the fugacity of CO_2. The values of the Henry's constants determined in this study are given in Table 4.3, together with some literature values of solvents used for the capture of CO_2. The higher the value of the Henry constant, the lower the solubility.

Table 4.3: Henry's law constants for the prepared hydrophobic DESs and literature values for ILs and conventional solvents.

	$H_{2,1}$ [MPa]		
Solvent	298.15 K	308.15 K	318.15 K
DecA:N_{4444}–Cl (2:1)	7.55 ± 0.08	8.74 ± 0.04	10.71 ± 0.35
DecA:N_{8881}–Br (2:1)	7.15 *	7.98 *	9.43 *
DecA:N_{8881}–Cl (2:1)	7.18 *	8.27 *	- **
DecA:N_{8888}–Br (2:1)	6.26 ± 0.07	7.15 ± 0.01	8.49 ± 0.16
DecA:N_{8888}–Cl (2:1)	6.17 ± 0.20	6.96 ± 0.07	8.42 ± 0.14
DecA:N_{8888}–Cl (1.5:1)	5.90 ± 0.09	6.55 ± 0.07	7.70 ± 0.09
Urea:choline chloride (2:1)[111]	-	-	15.1
Lactic acid:N_{4444}–Cl (2:1)[32]	-	14.46	-
[C_4mim][BF_4][110]	5.90 ± 0.26	-	8.86 ± 0.19
[C_4mim][TF_2N][110]	3.30 ± 0.03	-	4.87 ± 0.09
Selexol[123]	3.57	-	5.62
Heptane[124]	8.43	-	-
Benzene[124]	10.4	-	-

* only measured one time, ** not measured

The results in Table 4.3 show that the hydrophobic DESs have a much higher solubility of CO_2 than hydrophilic DESs and the conventional solvents heptane and benzene. The results for CO_2 solubility are comparable to [C_4mim][BF_4], which has the second best solubility of CO_2 in ILs. The results show that the IL [C_4mim][TF_2N] and the industrial process selexol still outperform the hydrophobic DESs. However, it should be noted that these are only the first presented hydrophobic DESs. Improvements in these systems are still possible and should be made.

4.4.5 PC-SAFT modeling of the CO_2 solubilities

For further investigations of CO_2 solubilities in hydrophobic DESs, a model that enables to predict the solubilities of CO_2 would allow for fast screening. In this chapter it was chosen to test the PC-SAFT model based on the 'pseudo-pure' approach for the DESs DecA:$N_{4444}-Cl$, DecA:$N_{8888}-Br$ (2:1), DecA:$N_{8888}-Cl$ (2:1) and DecA:$N_{8888}-Cl$ (1.5:1) as previously described by Zubeir *et al.*[114] An advantage of the 'pseudo-pure' approach is the fact that only liquid density data is needed to obtain different parameters for the model. These parameters are the segment number ($m_{\mathrm{seg,i}}$), the temperature-independent segment diameter (σ_{i}) and the dispersion-energy parameter ($u_{\mathrm{i}}/\mathrm{k_B}$).

The fits for the densities are shown in Figure 4.4. They show slight overestimation at low temperatures and slight underestimation at high temperatures.

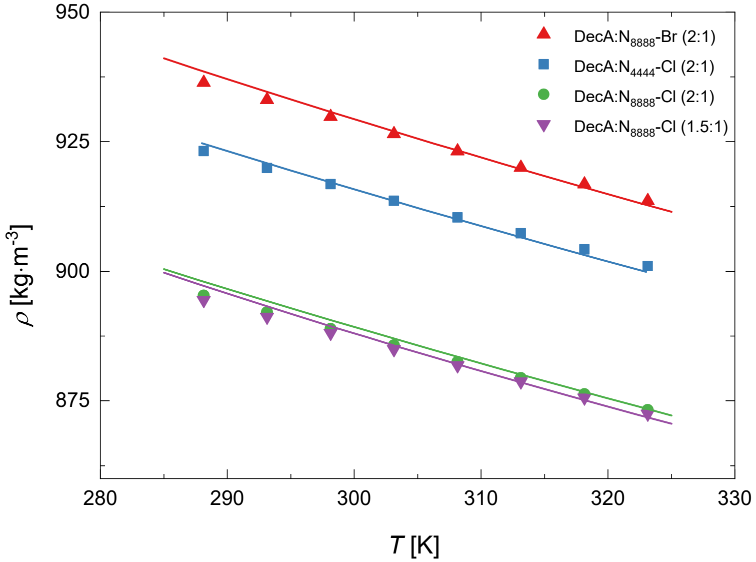


Figure 4.4: Densities of Deca:$N_{8888}-Br$ (2:1), Deca:$N_{4444}-Cl$ (2:1), Deca:$N_{8888}-Cl$ (2:1) and Deca:$N_{8888}-Cl$ (1.5:1), as function of the temperature. The symbols represent the experimental data and the solid curves represent the PC-SAFT results.

The absolute average relative deviation, AARD (%), between experimental densities of the DESs and PC-SAFT correlation are calculated via Equation 4.2.

$$\mathrm{AARD}\,(\%) = \frac{1}{n}\sum\left|\frac{y_i^{\mathrm{exp}} - y_i^{\mathrm{calc}}}{y_i^{\mathrm{calc}}}\right| \cdot 100\% \tag{4.2}$$

In this equation y is a property determined via experiments and modeling of component i, while n is the number of experimental data points. The AARD (%) DecA:$N_{4444}-Cl$ (2:1), DecA:$N_{8888}-Br$ (2:1), DecA:$N_{8888}-Cl$ (2:1) and DecA:$N_{8888}-Cl$ (1.5:1) were 0.008, 0.103, 0.150 and 0.135, respectively. The AARD(%) show a good agreement between the densities determined via experiments and PC-SAFT.

The pure-component PC-SAFT parameters for CO_2 were obtained from literature.[119] The parameters $m_{\mathrm{seg,i}}$, σ_{i}, and $u_{\mathrm{i}}/k_{\mathrm{B}}$ are presented in Table 4.4, while N_{site} was set to 1+1, $\epsilon^{\mathrm{AiBi}}/\mathrm{kB}$ to 0 and κ^{AiBi} to 0.1. For the hydrophobic DESs, N_{site} was set to 1+1, $\epsilon^{\mathrm{AiBi}}/\mathrm{kB}$ to 5000 and κ^{AiBi} to 0.1. Induced association according to Kleiner and Sadowski[125] was applied for the CO_2+DES mixtures. The pure component parameters, $m_{\mathrm{seg,i}}$, σ_{i}, and $u_{\mathrm{i}}/k_{\mathrm{B}}$ were fitted to their liquid densities.[95]

Table 4.4: PC-SAFT pure component parameters for CO_2 and DESs. The parameters for CO_2 and the two hydrophilic DESs were obtained from literature.

Component	M [$\mathrm{g\,mol^{-1}}$]	$m_{\mathrm{seg,i}}$	σ_{i} [Å]	$u_{\mathrm{i}}/k_{\mathrm{B}}$ [K]
CO_2	44.01	2.073	2.7852	169.21
DecA:N_{4444} – Cl (2:1)	207.41	10.908	3.1535	311.30
DecA:N_{8888} – Br (2:1)	297.04	15.482	3.1583	317.42
DecA:N_{8888} – Cl (2:1)	282.22	15.322	3.1533	307.11
DecA:N_{8888} – Cl (1.5:1)	304.23	14.800	3.2400	382.09
LA:TBA-Cl (2:1)[114]	152.69	11.730	2.6760	303.76
LA:TBA-Cl (3:1)[114]	137.04	10.533	2.6760	338.00

Table 4.4 shows the comparison between PC-SAFT parameters for hydrophilic and hydrophobic DESs, determined in this work. It can be observed that the three pure component PC-SAFT parameters ($m_{\mathrm{seg,i}}$, σ_{i}, and $u_{\mathrm{i}}/k_{\mathrm{B}}$) are in the same order of magnitude for the hydrophobic and hydrophilic DESs, as was expected.

Figure 4.5 shows the correlation between the molar mass (M_{w}) of the DESs and their segment volume $\left(m_{\mathrm{seg}} \cdot \sigma^3\right)$. The higher the M_{w} of the DES, the higher $m_{\mathrm{seg}} \cdot \sigma^3$. For comparison, the hydrophilic DESs modeled by Zubeir *et al.*[114] are also included in Figure 4.5. A strong linear correlation with a R^2 of 0.9973 is found between the $m_{\mathrm{seg}} \cdot \sigma^3$ and M_{w}. This linear correlation allows us to predict the segment number for other DESs.

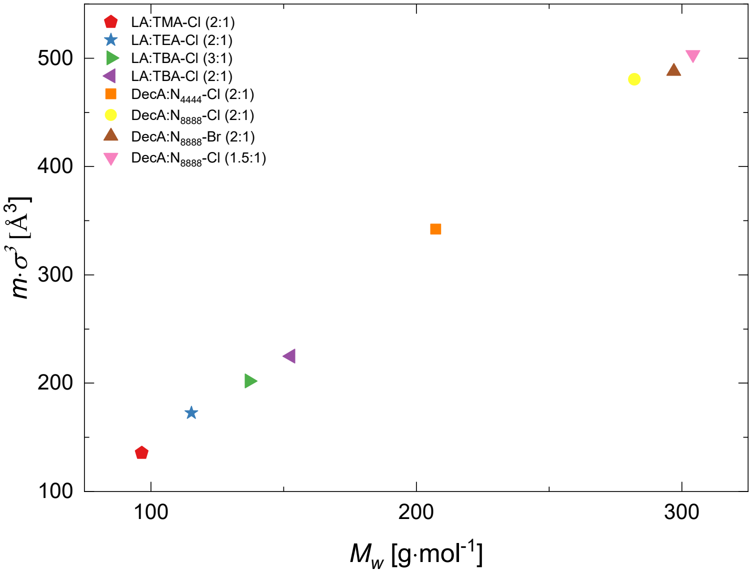


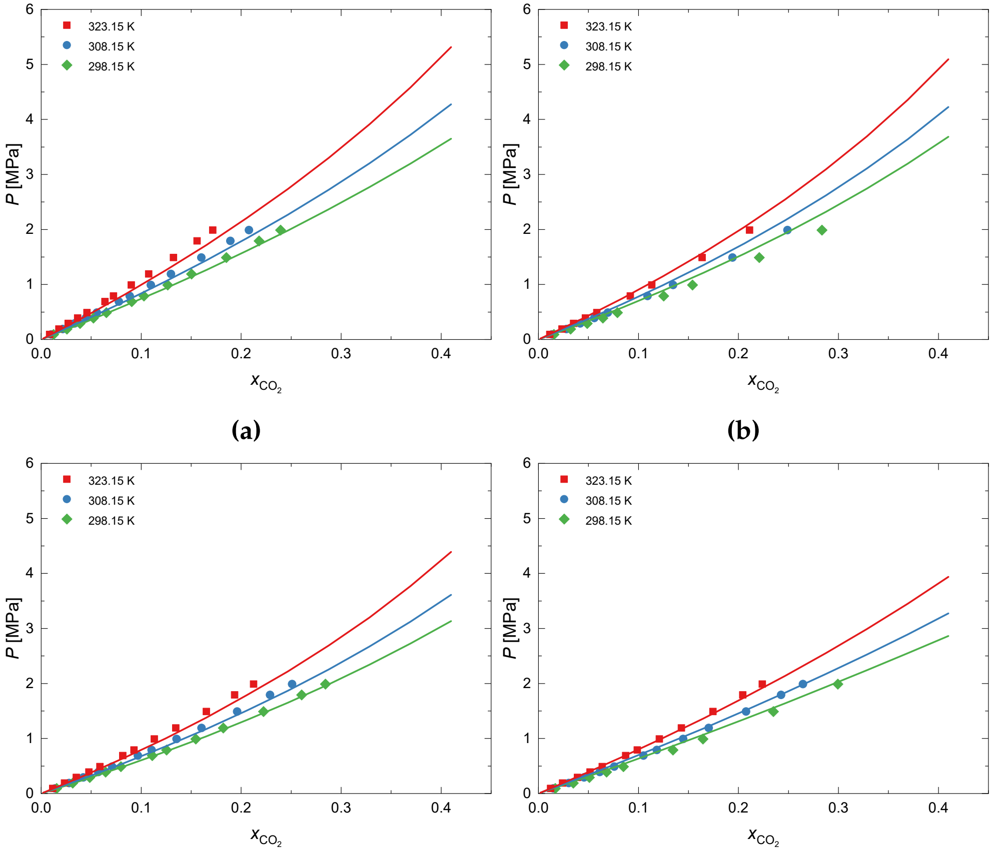
Figure 4.5: Correlation between the molecular weight (M_w) and the segment volume ($m_\mathrm{seg} \cdot \sigma^3$) obtained with PC-SAFT from Table 4.4 for hydrophobic DESs modeled in this work and hydrophilic DESs modeled elsewhere.[114]

Based on the PC-SAFT parameters listed in Table 4.4, CO_2 solubilities were predicted for the considered hydrophobic DESs. For all DESs, the VLE data of the binary DES + CO_2 systems were predicted without adjusting any binary interaction parameter. Table 4.5 shows the percentage AARD (%) between the experimental and the predicted VLE of the DESs + CO_2 systems, which was determined with equation 4.2. Figures 4.6a to 4.6d show the VLE data of all hydrophobic DESs + CO_2 systems studied in this work.

Table 4.5: Absolute average relative deviation, AARD (%), of the VLE data at various temperatures for the examined DES + CO_2 systems.

Component	T [K]	Number of data points	k_{ij}	AARD (%)
DecA:N_{4444}−Cl (2:1)	298.15	12	0	3.92
	308.15	12	0	7.60
	323.15	12	0	10.94
DecA:N_{8888}−Br (2:1)	298.15	9	0	12.01
	308.15	9	0	7.37
	323.15	9	0	4.15
DecA:N_{8888}−Cl (2:1)	298.15	12	0	4.01
	308.15	12	0	4.67
	323.15	12	0	7.93
DecA:N_{8888}−Cl (1.5:1)	298.15	11	0	8.70
	308.15	11	0	5.08
	323.15	11	0	2.27

PC-SAFT underestimates the CO_2 solubilities in the DES DecA:N_{4444}−Cl (2:1), where the AARD (%) increases for increasing temperatures. At 298.15 K the model slightly overestimates the experimental pressure. PC-SAFT overestimated the isotherms for the DecA:N_{8888}−Br (2:1) + CO_2 system. The overestimation increased with temperature. The predictions of PC-SAFT for the DES DecA:N_{8888}−Cl (2:1) + CO_2 show a good comparison with the experimental data at a temperature of 298.15 K and 308.15 K with an AARD (%) of 4.01% and 4.67%, respectively.[98] At 323.15 K the PC-SAFT underestimates the system pressure of DES + CO_2 system resulting in a higher AARD (%) of 7.93%. For the 1.5:1 molar ratio of the DES DecA:N_{8888}−Cl the predictions at 308.15 K and 323.15 K are reasonable to good with AARD (%) values of 5.08% and 2.27%, respectively. Underestimation and overestimation is caused by the fact that no interactions are taken into account as also shown in 4.5, k_{ij} is zero for all DESs and temperatures. This could improve the model.



(a) **(b)**

(c) **(d)**

Figure 4.6: VLE of different hydrophobic DES + CO_2 systems at three isotherms. (squares: 323.15 K, circles: 308.15 and diamonds: 298.15). The lines are results obtained with PC-SAFT using the parameters in Table 4.4. The following DESs are shown: (4.6a) DecA:$N_{4444}-Cl$ (2:1) + CO_2; (4.6b) DecA:$N_{8888}-Br$ (2:1) + CO_2; (4.6c) DecA:$N_{8888}-Cl$ (2:1) + CO_2; (4.6d) DecA:$N_{8888}-Cl$ (1.5:1) + CO_2.

4.5 Conclusions and outlook

In this chapter it is shown that hydrophobic DESs based on decanoic acid and quaternary ammonium salts have moderate to good CO_2 solubilities. The results show that the solubility occurs via physical absorption and depends on the molar volume of the DES. The higher the molar volume, the more CO_2 the DES can solubilize. Changing the anion has negligible effect on the solubility, while changing the methyl chain to an octyl chain increases the amount of CO_2 that can be absorbed, due to changes in molar volume.

Henry's law constants were determined to compare the CO_2 solubilities in the hydrophobic DESs to solubilities in ILs and conventional solvents. The results show that the DES DecA:$N_{8888}-Cl$ (1.5:1) can solubilize similar amounts of CO_2 as [C_4mim][BF_4], which is one of the most promising ILs used for the capture of CO_2.

The PC-SAFT modeling shows that reasonable to good predictions can be made of CO_2 solubilities in the hydrophobic DESs by estimating the parameters, for which only the liquid densities are needed. This allows for fast screening into even more promising hydrophobic DES for solubilizing CO_2, saving significant time compared to experimental methods.

Since these are the first results of CO_2 solubilities in hydrophobic DESs more research should be performed to find even more suitable hydrophobic DESs for CO_2 capture. DESs that have a higher solubility can be found via the use of the PC-SAFT model. Also, the solubility of components such as CH_4 in DESs should be tested in order to find distribution coefficients between the different components in natural gas.

4.6 Appendix

4.6.1 NMRs of the DESs

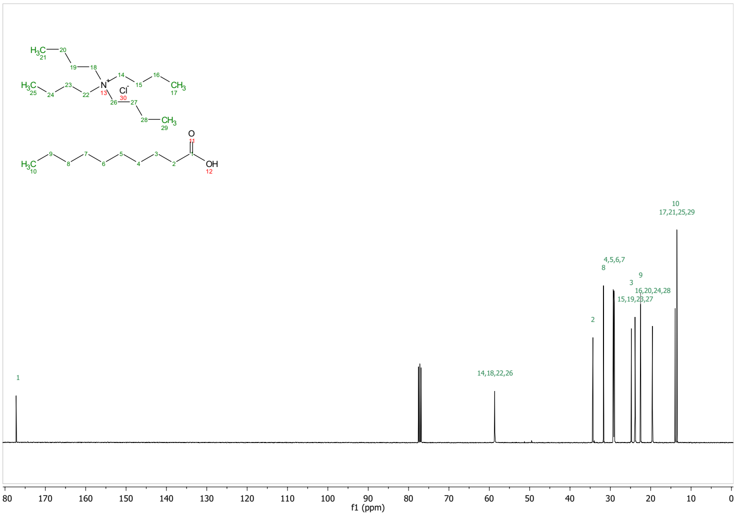


Figure 4.7: ^{13}C NMR of the DES decanoic acid with tetrabutylammonium chloride in a 2:1 ratio as prepared.

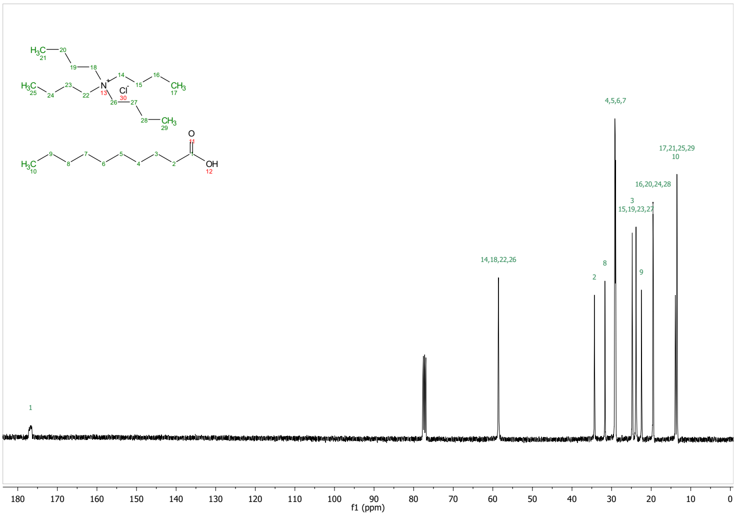


Figure 4.8: ^{13}C NMR of the DES decanoic acid with tetrabutylammonium chloride in a 2:1 ratio after CO_2 solubility measurements and regeneration.

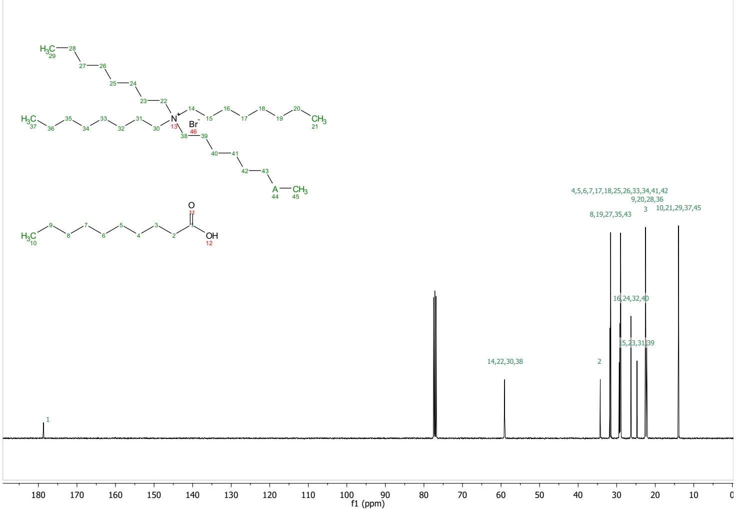


Figure 4.9: ^{13}C NMR of the DES decanoic acid with tetraoctylammonium bromide in a 2:1 ratio as prepared.

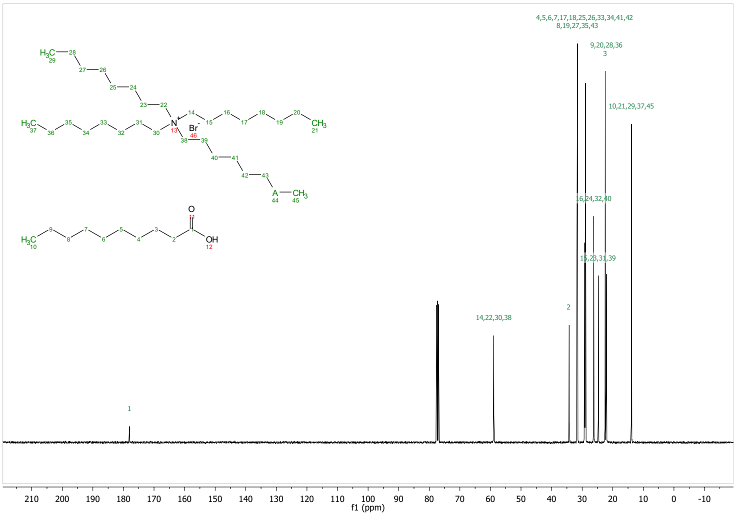


Figure 4.10: ^{13}C NMR of the DES decanoic acid with tetraoctylammonium bromide in a 2:1 ratio after CO$_2$ solubility measurements and regeneration.

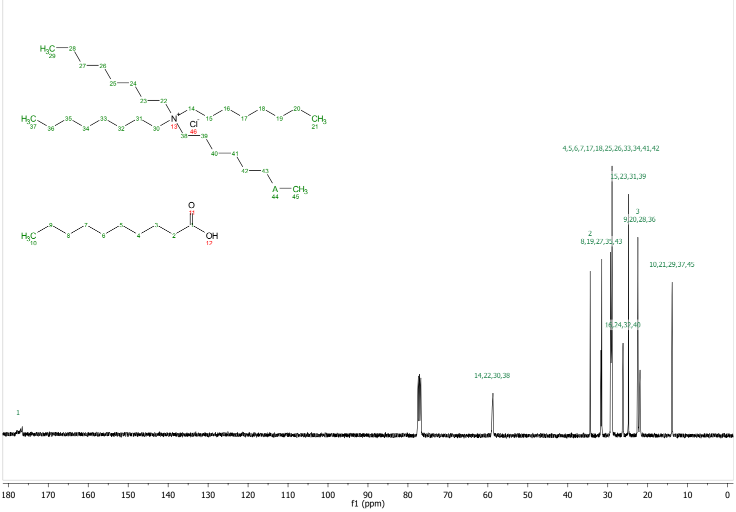


Figure 4.11: ^{13}C NMR of the DES decanoic acid with tetraoctylammonium chloride in a 2:1 ratio as prepared.

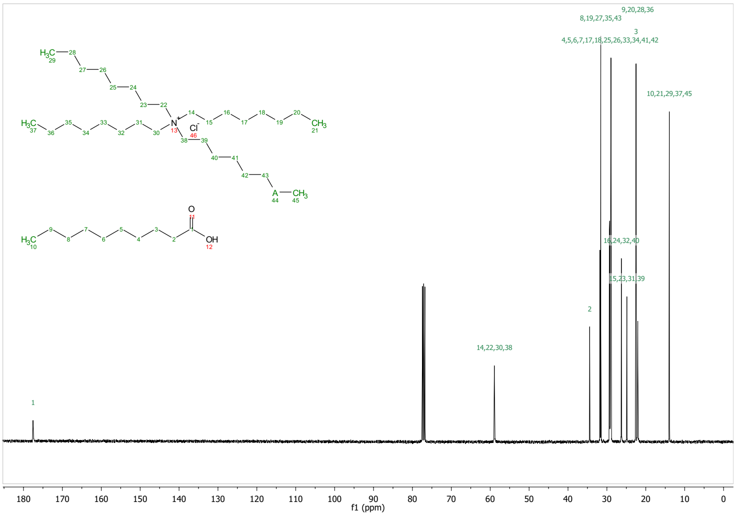


Figure 4.12: ^{13}C NMR of the DES decanoic acid with tetraoctylammonium chloride in a 2:1 ratio after CO_2 solubility measurements and regeneration.

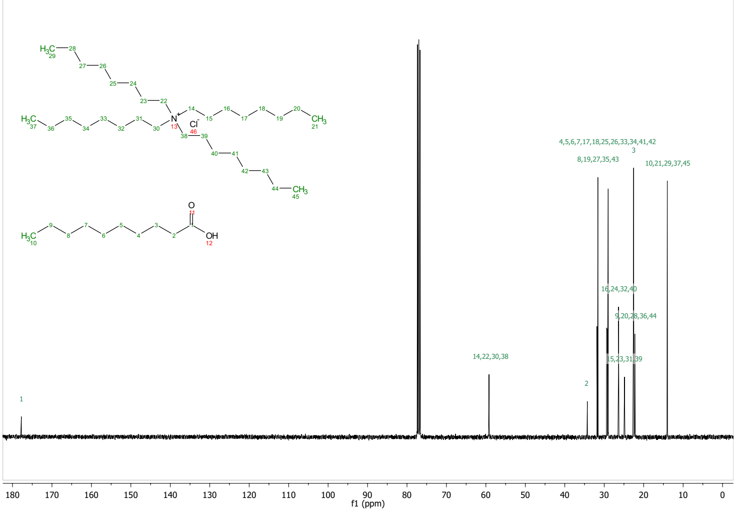


Figure 4.13: ^{13}C NMR of the DES decanoic acid with tetraoctylammonium chloride in a 1.5:1 ratio as prepared.

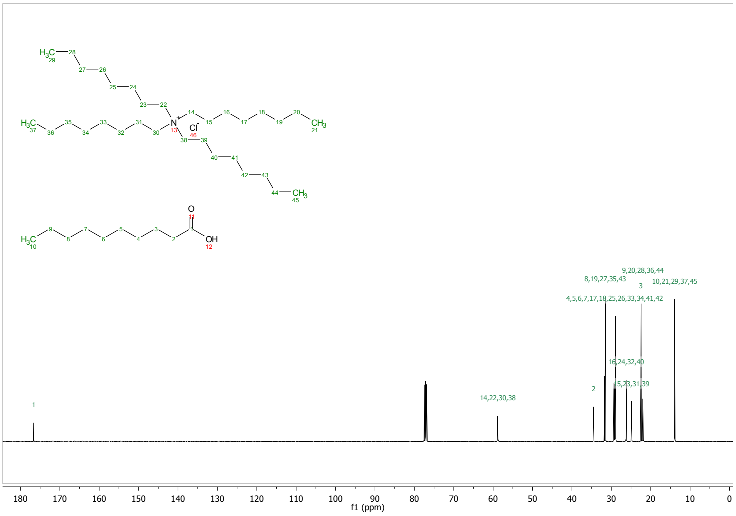


Figure 4.14: ^{13}C NMR of the DES decanoic acid with tetraoctylammonium chloride in a 1.5:1 ratio after CO_2 solubility measurements and regeneration.

Chapter 5

Metal Ion Removal from Water with Hydrophobic Deep Eutectic Solvents

Abstract

Hydrophobic deep eutectic solvents were used for the removal of metal ions from non-buffered water. It was shown that the extraction occurs via an ion exchange mechanism in which the transition metal ions could be extracted with high distribution coefficients, even for high Co^{2+} concentrations and low DES/water mass ratios. Maximum extraction efficiency could be reached within 5 s and regeneration of the DES was possible.

This chapter is a modified version of:
Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, *Chem. Commun.*, 2016, **52**, 11987-11990

5.1 Introduction

The contamination of water with high metal salt concentrations makes water non-potable, while for some metals (e.g. Cd, Pb, As) even traces are highly toxic.[126,127] To avoid this environmental and health issue, the removal of metal salts from water is of major importance. Moreover, their extraction from water can be of interest from an economical perspective, since certain metal salts are getting scarce (e.g. Pd, Au, Ag), making them expensive. For these reasons, it is important to remove metal salts from aquatic environments.

A generally accepted and often applied technique for the removal of metal salts from water is liquid–liquid extraction with hydrophobic solvents.[128] Extraction offers advantages over other methods such as the possibility of conducting the removal in a continuous mode, the use of rather easy to operate equipment, simple reactor design and the need for only small amounts of extractant.[129]

Most investigations into the extraction of metal salts from an aquatic environment have focused on the use of conventional organic water-immiscible solvents such as dodecane, toluene and kerosene. The main disadvantages of these solvents are their toxicity, volatility and flammability.[130]

A hydrophobic DES that could enable the removal of metal salts or metal ions from water is of interest for many industries. For example, in the pulp and paper industry this might introduce the removal of transition metals, such as Mn and Fe, from fibre suspensions prior to peroxide bleaching, which allows for replacing the use of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and other acidic environments.[131,132] Moreover, the newly developed DESs have the possibility to be used for regulating the final metal contents of dissolving pulp and for the removal of metal ions from wood raw material.[131,132] Furthermore, it might be of interest to investigate whether silica and calcium ions can be removed from water and/or from equipment, avoiding precipitations inside the equipment. Finally, it is interesting to investigate whether these DESs are usable in ion exchangers.

This chapter focuses on the extraction of different metal chloride salts from an aquatic environment using hydrophobic DESs. Studies into the extraction mechanism of hydrophobic ionic liquids (ILs) produced from fatty acids and quaternary ammonium salts indicated that the metal part of the metal salt forms complexes with the deprotonated acid groups, while negatively charged chloride interacts with the positively charged nitrogen of the IL.[106] Hence, a DES was chosen that consists of decanoic acid (DecA) and lidocaine (Lid) since it was recently shown that approximately 25 % of the decanoic acid/lidocaine DES in a 2:1 molar ratio was ionized.[77,78] The components DecA and Lid were used in 2:1, 3:1 and 4:1 molar ratios. The pH of the water phase was not changed to improve extraction efficiency as published recently for metal salts in acid solutions.[80] Thus, only metal salt and water were present in the aqueous phase, which to the best of our knowledge has not been investigated before. The measured distribution coefficients (D) for the ions of the metal chloride salts; cobalt ($CoCl_2$), nickel ($NiCl_2$), iron ($FeCl_2$), manganese ($MnCl_2$), zinc ($ZnCl_2$), copper ($CuCl_2$), sodium (NaCl), potassium (KCl) and lithium (LiCl) were reported. Furthermore, different concentrations and DES/water mass ratios (ϕ_{DES}) were tested for the metal salt $CoCl_2$. Finally, the regeneration of the DESs was investigated.

5.2 Experimental section

5.2.1 Materials, preparation and metal salt extraction method

Materials

Decanoic acid (DecA) and lidocaine (Lid) were both purchased from Sigma-Aldrich with purities of >98 % and >99 %, respectively (see Figure 5.1 for the chemical structures of the components of the DESs). $CoCl_2 \cdot 6\,H_2O$ was ordered from Alfa Aesar with a purity of >98 %. $NiCl_2 \cdot 6\,H_2O$ and $MnCl_2 \cdot 2\,H_2O$ were supplied by Boom laboratory with purities of >99 %. $CuCl_2 \cdot 2\,H_2O$, NaCl and KCl were purchased from VWR Chemicals with purities of, respectively, >99 %, >99.99 % and >99.99 %. $FeCl_2 \cdot 4\,H_2O$ and LiCl (Merck) had purities >99 %, while $ZnCl_2$ was supplied by Sigma-Aldrich with a purity of >99 %. All chemicals were used as supplied.

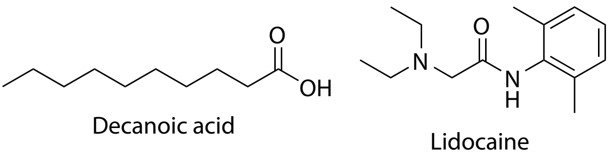


Figure 5.1: Chemical structure of the starting components of the DESs.

Preparation of the DES

The three DESs were all prepared by the following procedure. DecA (for DecA:Lid (2:1) 89.28 g, DecA:Lid (3:1) 103.20 g and DecA:Lid (4:1) 111.93 g) was weighed in a 250 mL flask and Lid (for DecA:Lid (2:1) 60.72 g, DecA:Lid (3:1) 46.80 g and DecA:Lid (4:1) 38.07 g) was added via a solid funnel or via weighing it in a weighing boat, after which it was added to the DecA. The flask was closed with a cap and parafilm was wrapped around the cap and the flask to ensure that the DESs were not able to uptake water. Next, the flask was heated to 308 K in an oil bath until a clear liquid appeared. The inside of the flasks was rinsed with the DES to ensure that all solids were in the liquid phase, after which the DESs were heated again to 308 K until a clear homogenous mixture was formed. Before use, the DESs were left, in their flask with the screw cap on it, overnight at room temperature to investigate if recrystallization occurred.

Determination of the water solubility in the DESs and their viscosity/density

The DESs were mixed with water to determine the amount of water they would take up. Approximately 23 g of DES was mixed with 23 mL of water in centrifuge tubes of 50 mL (CELLSTAR®), which were shaken in an IKA KS 4000 I incubating shaker and centrifuged for 30 min at 12.000 RPM in a Sigma 2-16 KL centrifuge. The top-phase, DES phase, was analyzed for its water content with a Karl-Fischer 899 coulometer titration apparatus. The density of the DES was measured with an Anton-Paar SVM 3000 Stabinger Viscometer and viscosity with an Anton Paar Physica MCR 301 rheometer. The bottom-phase was analyzed for its total organic carbon (TOC).

Metal salt extraction method

Five different stock solutions were prepared. Four stock solutions constituted of a single metal complex, being $CoCl_2{\cdot}6\,H_2O$, $FeCl_2{\cdot}4\,H_2O$, $MnCl_2{\cdot}2\,H_2O$, $NiCl_2{\cdot}6\,H_2O$ $ZnCl_2$, $CuCl_2{\cdot}2\,H_2O$, NaCl, KCl, LiCl. The specific reasons for this are listed below and these numbers correlate to the experiment numbers as depicted in Table 5.7: 1) The stock with $CoCl_2{\cdot}6\,H_2O$ was also used for further research into extraction times and regeneration. 2) For $FeCl_2{\cdot}4\,H_2O$ it was checked whether a precipitation would form as was shown in literature for ionic liquids (ILs). 3) $MnCl_2{\cdot}2\,H_2O$ showed from initial experiments the formation of a gel like DES phase. 4) Analysis showed that in some cases the values of sodium and potassium showed similar peaks in analysis with induced coupled plasma (ICP). 5) The stock with a combination of the salts was used to test the versatility and selectivity of the extraction method. The results of experiment 3 led to the exclusion of $MnCl_2$ from this stock. For all the experiments a concentration of $1.0\,\mathrm{g}\cdot\mathrm{L}^{-1}$ of metal ion was used. For experiment 5, the measurement of the chloride concentration after extraction was considered unreliable. The deviations were probably caused by the cumulative variations in distribution coefficients of the alkali cations.

For the extraction, first an approximate amount of 10 g of DES was weighed and added to a centrifuge tube (CELLSTAR®) of 50 mL to which 10 mL of metal salt solution was added. The mixture was shaken for 1 h on a Heidolph multireax multivortex shaker with 1800 RPM (T = 295 K) and centrifuged for 10 min at 3000 RPM with a Beckmann Coulters centrifuge. The water phase was analyzed with TOC for the amount of organic substance, ion chromatography (IC) for the chlorides and ICP for the metal ions. It should be noted that sampling of the water phases was extremely difficult, which could have influenced the results of the TOC values slightly.

Determination of the volumes of the water phase

The volumes of the water phase were determined by estimating the heights of the two phases by the use of a ruler. The volume of the water phase after extraction was calculated by multiplying the ratio between the two volumes based between the two bars times that volume.

Regeneration experiment

For the regeneration experiment first $1.0\,\mathrm{g} \cdot \mathrm{L}^{-1}$ Co^{2+} from H_2O was extracted as also mentioned in paragraph 5.2.1 The DES phase was sampled after centrifugation for further use. In the regeneration step 10 g of 0.1 M sodium oxalate ($Na_2C_2O_4$) was added to 10 g of DES with metal ions in it. This mixture was shaken for 1 h on a Heidolph multireax multivortex shaker with 1800 RPM (T = 295 K) and centrifuged for 10 min at 3000 RPM with a Beckmann Coulters centrifuge. After the centrifugation step the DES and H_2O phase were separated, after which again an extraction experiment was conducted as explained in paragraph 5.2.1.

5.2.2 Analytical methodologies

Karl-Fischer

Karl Fischer analysis with an 899 Coulometer (Metrohm Karl Fischer) was used for measuring the water content of the DESs after preparation and after mixing with water.

Density

An Anton Paar SVM 3000 Stabinger Viscometer was used for measuring the density of the developed DESs between 293.15 to 323.15 K at atmospheric pressure. In the range of 288.15 to 378.15 K the temperature uncertainty is listed as 0.02 K. The absolute uncertainty of the density is approximately $0.5\,\mathrm{kg\cdot m^{-3}}$.

Viscosity

The viscosity between 293.15 to 323.15 K was measured with an Anton Paar Physica MCR 301 rheometer.

Thermogravimetric analysis (TGA)

A thermogravimetric analyzer (Perkin Elmer TGA 4000) was used for studying the decomposition temperature of the DESs. The mass of the samples varied from 7 to 13 mg. The precision and the sensitivity of the balance are ± 0.01 % and 1 µg. For the heating of the samples a ceramic crucible was used. The conditions for heating were a heating rate of $10\,\mathrm{K\cdot min^{-1}}$ over a temperature range of 303 to 873 K where a continuous flow of nitrogen, $20\,\mathrm{mL\cdot min^{-1}}$, with a pressure of 0.2 MPa was used.

Nuclear magnetic resonance (NMR) of the DESs

Nuclear Magnetic Resonance was used for recording both hydrogen (^{1}H) and carbon (^{13}C) NMR spectra. A Bruker 400 automatic NMR was used. The DES samples were added to an 8″ Wilmad NMR tube (outer diameter of 5 mm) and mixed with deuterated chloroform ($CDCl_3$). The spectra for the ^{13}C NMR were recorded in 1000 scans with a relaxation time of 3 s. The ^{1}H NMR were recorded with 128 scans and a relaxation time of 3 s. The NMR spectra were used as obtained and analyzed with MestreNova (version 9.1.0-14011) and ChemBiodraw (version 14.0.0.117).

Nuclear magnetic resonance (NMR) of the water phases after the extraction experiments

Undiluted samples of the water phase after extraction were studied using a ^{1}H NMR water suppressing pulse sequence. The samples were each added to an 8″ Wilmad NMR thin-walled tube (outer diameter of 5 mm) and equipped with an 8″ Wilmad insert with an inner capacity of 60 µL, stem height of 50 mm and stem outer diameter of 2 mm filled with D_2O as lock reference. The water peak was suppressed by using a NOESY-presaturation pulse sequence, Bruker 1D noesygppr1d, at the peak maximum of the water peak (WATER program in Bruker TopSpin^{tm}).

The spectra were normalized setting the two protons from the lidocaine molecule, $(CH_3-CH_2)_2-N-\underline{\mathbf{CH2}}-(C=O)-NH-R$, to 2.00. The ratio between DecA and Lid was calculated by dividing the resulting integral of the CH_3 of DecA by 3.

Fourier transform infrared (FTIR)

A PerkinElmer Spectrum Two spectrometer equipped with a Spectrum Two UATR (universal attenuated total reflectance) module was used for measuring the Fourier transformed infrared (FTIR) spectra. The measurements were conducted over a wavenumber range of 450-4000 cm^{-1}. For the pure component 4 scans were used, while 16 scans were used for measuring the DESs. Of every sample a background spectrum was recorded, with which a baseline correction was performed with the PerkinElmer Spectrum software (application version 10.03.08.0135, 2012).

Ion chromatography

The chloride concentrations were measured with a Metrohm 761 Compact ion chromatograph (IC). The column in the IC is a Metrohm Metrosep A Supp 5, 150/4.0 mm. The pre-column is a Metrohm Metrosep A Supp 4/5 Guard. The conductivity detector, chemical suppressor from Metrohm, CO_2 suppressor (Metrohm, type 853) are all built into the ion chromatograph.

The reagents of the mobile phase are 3.2 mM sodium carbonate and 1 mM sodium bicarbonate solution in combination with 1 % of acetone. The suppressor liquids are 0.5 M H_3PO_4 with 1 % acetone and Milli-Q water with 1 % of acetone.

The mobile phase had a flow of $0.7\,\mathrm{mL \cdot min^{-1}}$ and the flow of the suppressor solutions had a flow of $0.4\,\mathrm{mL \cdot min^{-1}}$. The injection volume is 20 µL and the runtime is 20 min. The detection limit is 0.05-0.10 $\mathrm{mg \cdot L^{-1}}$, while the upper limit is $80\,\mathrm{mg \cdot L^{-1}}$.

Induced coupled plasma (ICP)

The ICP is a Perkin Elmer from the type Optima 5300 DV with a Perkin Elmer autosampler of the type ESI-SC-4 DX fast. The watercooler used for the ICP is the type 6106 P from Polyscience. The internal standard solution is $10\,\mathrm{mg \cdot L^{-1}}$ Yttrium and the rinse solution is 2 % nitric acid. The detection limit varies from 25-750 $\mathrm{\mu g\,L^{-1}}$ and the upper limit is 10000 $\mathrm{\mu g\,L^{-1}}$. The '>' in Table 5.7 means that the values for that metal ion were lower than the detection limit.

Total organic carbon (TOC)

A Shimadzu TOC-L_{CPH} with an ASI-L Autosampler was used for the analysis of the total organic carbon (TOC) in the water phase. The reagents that are used are 2 M hydrochloric acid and 25 % phosphoric acid. The detection limit is $80\,\mathrm{mg \cdot L^{-1}}$.

5.3 Results and discussion

5.3.1 Physicochemical properties

Table 5.1: Physicochemical properties of the investigated DESs, where ρ is the density and η is the viscosity measured at 298 K before mixing with water. w_{H_2O} are the water contents measured at room temperature (295 ± 1 K) before mixing with water. T_d is the degradation temperature of the DES.

DES	w_{before,H_2O} [wt %]	$\rho_{\text{before},H_2O}$ [$kg \cdot m^{-3}$]	$\eta_{\text{before},H_2O}$ [$mPa \cdot s$]	T_d [K]
DecA:Lid (2:1)	731.3 ± 4.2	958.25 ± 0.05	237.5 ± 4.5	465.6
DecA:Lid (3:1)	280.1 ± 4.8	949.70 ± 0.0	208.5 ± 3.5	455.7
DecA:Lid (4:1)	242.7 ± 3.2	941.90 ± 0.0	142.0 ± 2.0	459.8

Table 5.2: Physicochemical properties of the investigated DESs, where ρ is the density and η is the viscosity measured at 298 K after mixing with water. w_{H_2O} are the water contents measured at room temperature (295 ± 1 K) after mixing with water. C_{DES} in water is the concentration of DES in the water phase after mixing determined with TOC.

DES	w_{after,H_2O} [wt %]	ρ_{after,H_2O} [$kg \cdot m^{-3}$]	η_{after,H_2O} [$mPa \cdot s$]	C_{DES} [$mg \cdot g^{-1}$]
DecA:Lid (2:1)	20.3 ± 0.3	980.0 ± 0.0	106.0 ± 1.0	16.1
DecA:Lid (3:1)	9.2 ± 0.01	961.35 ± 0.05	124.5 ± 1.5	10.6
DecA:Lid (4:1)	7.0 ± 0.01	950.95 ± 0.5	103.0 ± 1.0	7.9

Various physicochemical properties of the synthesized hydrophobic DESs were investigated (Table 5.1 and 5.2). The results show that the water content for the prepared DESs varied from approximately 243 ppm to 731 ppm. Furthermore, the water content decreased with an increase of the decanoic acid to lidocaine ratio. Thus, the more decanoic acid is present in the DESs, the more hydrophobic it is. The densities of the DES were lower than that of water, but very close to it. The operation window was determined via comparing the melting temperature and the degradation temperature. In the literature a glass transition temperature was given, which was 207 K.[78] The degradation temperatures were measured and are between 445.2 and 466.2 K. The difference between these two ensures the use of the three DESs at a large temperature operating window. NMR analyses showed that the two components of the hydrophobic DESs underwent no chemical reaction (Appendix 5.5.1). The density after mixing with water varied only slightly, while the viscosity dropped considerably. This drop can be explained by the increase of the water content after mixing with water, which rose to 7-20 wt %. The concentration of organic substance in the water phase after mixing with water varied from $8\,\mathrm{mg}\cdot\mathrm{L}^{-1}$ to $16\,\mathrm{mg}\cdot\mathrm{L}^{-1}$. These values are lower than the amount of organics transferred to the water phase for the hydrophobic DESs composed of decanoic acid and quaternary ammonium salts.

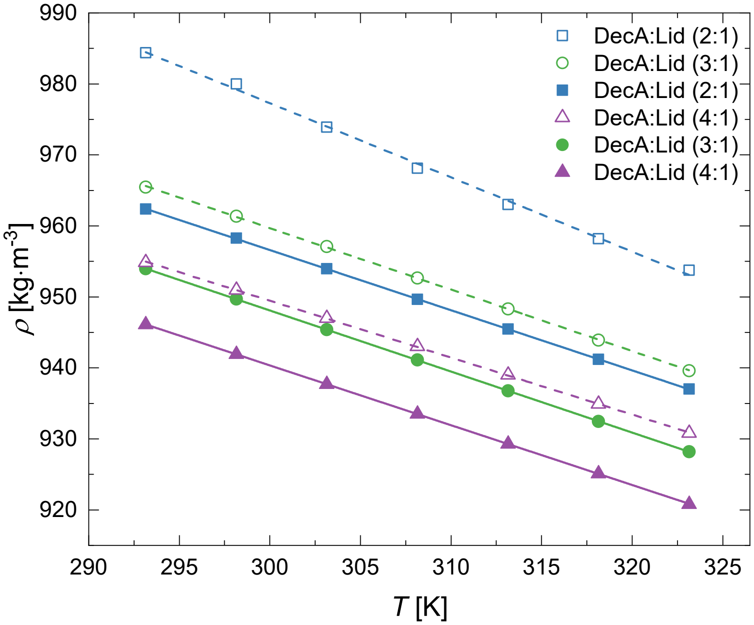


Figure 5.2: Densities as a function of temperature. The solid curves depict the DESs before mixing with water, while the dashed curves are the DESs after mixing with water.

The densities and viscosities of the pure DESs and the DESs after mixing with water over a temperature range are plotted in Figures 5.2 and 5.3. Both the densities and the viscosities decrease over an increase of temperature. A correlation for the density that is often used for ILs,[88,89] is given in Equation

5.1 as:

$$\rho = a + bT \tag{5.1}$$

Table 5.3: Fitting parameters of the densities before mixing with H_2O (equation 5.1).

DES	a $[\mathrm{kg} \cdot \mathrm{m}^{-3}]$	b $[\mathrm{kg} \cdot \mathrm{m}^{-3} \cdot \mathrm{K}^{-1}]$
DecA:Lid (2:1)	1211.44	-0.85
DecA:Lid (3:1)	1206.11	-0.86
DecA:Lid (4:1)	1192.99	-0.84

Table 5.4: Fitting parameters of the densities after mixing with H_2O (equation 5.1).

DES	a $[\mathrm{kg} \cdot \mathrm{m}^{-3}]$	b $[\mathrm{kg} \cdot \mathrm{m}^{-3} \cdot \mathrm{K}^{-1}]$
DecA:Lid (2:1)	1290.79	-1.05
DecA:Lid (3:1)	1220.07	-0.87
DecA:Lid (4:1)	1190.56	-0.80

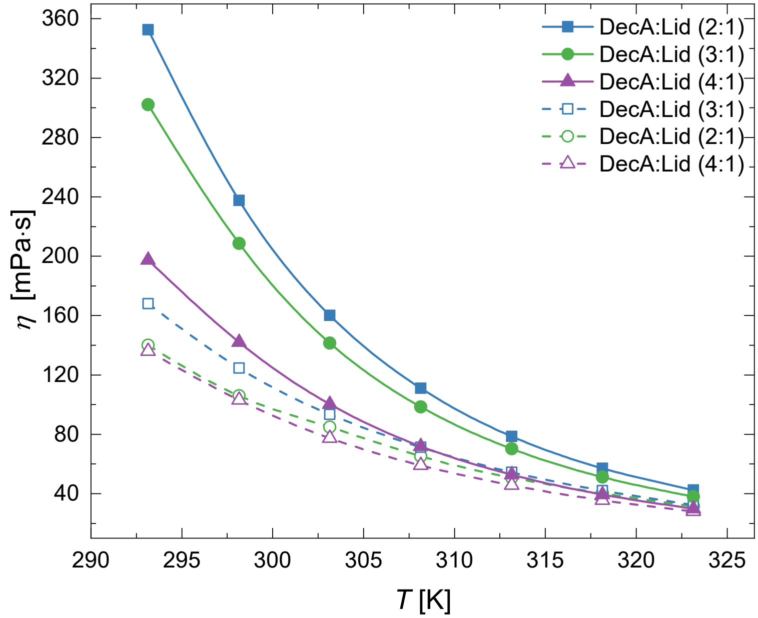


Figure 5.3: Viscosities as a function of temperature. The solid symbols and curves depict the DESs before mixing with water, while the dashed symbols and curves are the DESs after mixing with water.

The following expression for the viscosities is often used for ILs:[88,89]

$$\eta = A_\eta \cdot \exp \frac{B_\eta}{T - C_\eta} \tag{5.2}$$

Table 5.5: Fitting parameters of the Vogel-Fulcher-Tammann for the DESs before mixing with water (Equation 5.2).

DES	A_η [mPa · s]	B_η [K]	C_η [K]
DecA:Lid (2:1)	6.84×10^{-3}	1364.38	-167.46
DecA:Lid (3:1)	4.18×10^{-3}	1509.29	-158.33
DecA:Lid (4:1)	6.37×10^{-3}	1426.74	-155.32

Table 5.6: Fitting parameters of the Vogel-Fulcher-Tammann equation for the DESs after mixing with water (Equation 5.2).

DES	A_η [mPa · s]	B_η [K]	C_η [K]
DecA:Lid (2:1)	8.39×10^{-4}	2621.16	-75.20
DecA:Lid (3:1)	9.52×10^{-3}	1496.42	-140.18
DecA:Lid (4:1)	1.19×10^{-3}	2250.66	-99.94

The density and viscosity can be described accurately using equation 5.1 and 5.2 for the three hydrophobic DESs, both before and after mixing with water. As expected, the densities after mixing with water increase, while the viscosities decrease.

5.3.2 Extraction experiments

The distribution coefficients of the metal ions over the water and hydrophobic DES phases were determined using five separate experiments and are presented in Table 5.7. For all experiments reported in Table 5.7 an initial concentration of 1.0 $\mathrm{g \cdot L^{-1}}$ metal ion was used. The measured D values were calculated based on analysis of the water phase using equation 5.3:

$$D = \frac{C^{\mathrm{aq}}_{\mathrm{ion},0} - C^{\mathrm{aq}}_{\mathrm{ion},1} \cdot \frac{V^{\mathrm{aq}}_1}{V^{\mathrm{aq}}_0}}{C^{\mathrm{aq}}_{\mathrm{ion},0}} \tag{5.3}$$

Table 5.7: Distribution coefficients (D) of metal cations and chloride anions over the hydrophobic DESs and water phases. For $D \rightarrow 0$, the ion remains in the aqueous phase, while the ion is completely extracted into the DES when $D \rightarrow 1$. The pH values of the aqueous phase before and after extraction can be found in Table 5.8 and 5.9.

		DecA:Lid (2:1)	DecA:Lid (3:1)	DecA:Lid (4:1)
Exp 1.	Co^{2+}	$> 0.996 \pm 0.001$	$> 0.996 \pm 0.001$	0.983 ± 0.002
	Cl^-	0.113 ± 0.002	0.078 ± 0.008	0.101 ± 0.0059
Exp 2.	Fe^{2+}	$> 0.992 \pm 0.001$	$> 0.991 \pm 0.001$	$> 0.991 \pm 0.001$
	Cl^-	0.197 ± 0.003	0.080 ± 0.001	0.113 ± 0.007
Exp 3.	Mn^{2+}	$> 0.992 \pm 0.001$	$> 0.991 \pm 0.001$	0.983 ± 0.004
	Cl^-	0.086 ± 0.002	0.081 ± 0.027	0.065 ± 0.011
Exp 4.	K^+	$> 0.457 \pm 0.001$	$> 0.397 \pm 0.001$	$> 0.457 \pm 0.001$
	Co^{2+}	$> 0.141 \pm 0.001$	$> 0.078 \pm 0.031$	$> 0.072 \pm 0.002$
Exp 5.	Co^{2+}	0.990 ± 0.001	0.946 ± 0.012	$> 0.777 \pm 0.008$
	Ni^{2+}	$> 0.996 \pm 0.001$	0.983 ± 0.001	0.880 ± 0.004
	Zn^{2+}	$> 0.995 \pm 0.001$	$> 0.995 \pm 0.001$	$> 0.995 \pm 0.001$
	Cu^{2+}	$> 0.996 \pm 0.001$	$> 0.996 \pm 0.001$	$> 0.996 \pm 0.001$
	Na^+	0.195 ± 0.001	0.140 ± 0.009	0.127 ± 0.040
	K^+	0.211 ± 0.028	0.161 ± 0.018	0.134 ± 0.005
	Li^+	0.266 ± 0.015	0.166 ± 0.001	0.128 ± 0.036

As shown in Table 5.7, most metal cations are extracted with high efficiencies ($D \rightarrow 1$). The experiments with only single metal salts in the water phase all show high D for the cationic metal ions, except for K^+, which can be explained by the preference of fatty acids to bind with transition metals and not with alkali metals.[133] Two observations should be mentioned.

Some small precipitations were observed in the water phase after extraction of Fe^{2+}, which can be explained by the fact that it precipitates at higher pH.[106] After extraction of Mn^{2+} the DES phase formed a gel/solid like phase, which is most likely caused by the interaction of the manganese cation with one of the constituents of the DES. For K^+, the reported hydrophobic DESs show a decrease in D with an increase of the decanoic acid to lidocaine ratio. This might be caused by the increase of hydrophobicity with an increase of decanoic acid in the DES. The experiment in which a combination of metal ions is extracted, experiment 5, shows high *D* for all transition metal ions, although the *D* values of Ni^{2+} and Co^{2+} decrease with an increase of the decanoic acid to lidocaine ratio. Furthermore, it can be observed that the extraction of the alkali metal ions in such a mixture of metal ions is rather low. This was already expected from the literature on the extraction of metal salts with ILs.[106,133]

Table 5.8: pH of the water phase before the extraction.

Metal salt present in the water phase	pH
$CoCl_2$	5.471
$FeCl_2$	2.848
$MnCl_2$	5.787
$CoCl_2$, $NiCl_2$, $ZnCl_2$, $CuCl_2$, NaCl, KCl, LiCl	4.372

Table 5.9: pH of the water phase after the extraction. For the combination experiment the following metal salts were extracted: $CoCl_2$, $NiCl_2$, $ZnCl_2$, $CuCl_2$, NaCl, KCl, LiCl.

Metal salt	pH DecA:Lid (2:1)	pH DecA:Lid (3:1)	pH DecA:Lid (4:1)
$CoCl_2$	6.306	5.740	5.184
$FeCl_2$	6.829	6.324	5.838
$MnCl_2$	6.773	6.278	5.792
$CoCl_2$, $NiCl_2$, $ZnCl_2$, $CuCl_2$, NaCl, KCl LiCl	6.772	6.295	5.806

Table 5.8 shows the pHs of the water phase upon addition of metal salts. The addition of metal salts to the water phase resulted in the decreases of pH. Upon removal of the metal salts the pH increased as is clearly given in Table 5.9. The higher the DecA:Lid molar ratio, the smaller the change in pH.

5.3.3 Variation in initial Co^{2+} concentration

Figure 5.4 shows that with an increase in the concentration of the metal ion Co^{2+}, D decreases. The higher the decanoic acid to lidocaine ratio, the higher the decrease in D.

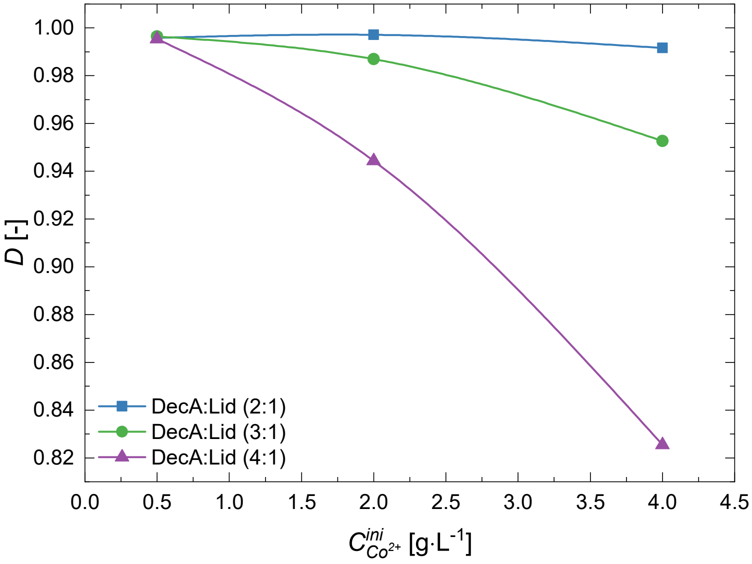


Figure 5.4: Distribution coefficient (D) with increasing concentration of Co^{2+}. The curves are added for clarification purposes.

For the chloride ions it was found that the D is small, which was not expected from previous research into the extraction mechanism of metal salts with similar fatty acid based ILs.[10,106] The low distribution coefficient of the DESs for the extraction of chloride ions may be explained by the interaction of the protonated lidocaine with chloride anions. Most likely, lidocaine hydrochloride is formed, which has a higher water solubility in comparison to lidocaine itself ($50\,\mathrm{mg \cdot mL^{-1}}$ for lidocaine chloride vs. $0.41\,\mathrm{mg \cdot mL^{-1}}$ for lidocaine). Thus, upon extraction of the metal ion into the DES phase, protonated lidocaine is transferred simultaneously to the water phase (forming lidocaine hydrochloride), which is an ion exchange process, as presented by Equation 5.4 and 5.5:

$$\mathrm{DecAH_{org} + DecAH_{org} \leftrightarrow DecA^{-}_{org} + LidH^{+}_{org}} \tag{5.4}$$

$$2\mathrm{LidH}^{+}_{\mathrm{org}} + \mathrm{M}^{2+}\mathrm{Cl}^{-}_{2,\mathrm{aq}} \leftrightarrow 2\mathrm{LidH}^{+}\mathrm{Cl}^{-}_{\mathrm{aq}} + \mathrm{M}^{2+}_{\mathrm{org}} \tag{5.5}$$

5.3.4 TOC values over a variation of initial Co^{2+} concentration

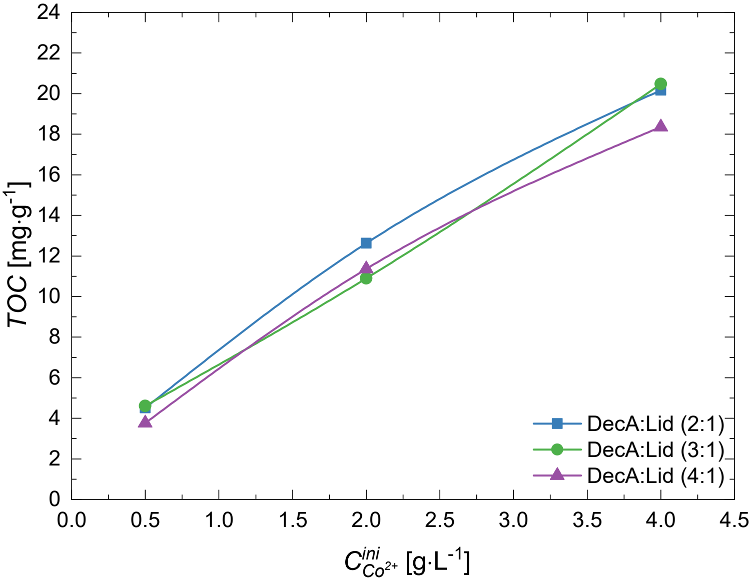


Figure 5.5: TOC values over the initial concentration of Co^{2+} in the water phase. The curves are added for clarification purposes.

This hypothesis was tested by varying the initial concentration of the metal ion to investigate if the concentration of the total organic carbon (TOC) in the water phase increased with an increasing amount of Co^{2+}. The change in TOC values with initial Co^{2+} concentration, as shown in Figure 5.5, supports that most likely Co^{2+} is exchanged with the positively charged lidocaine. To strengthen this assumption, NMR analysis was performed on the water phases after extraction (Appendix 5.5.2). Table 5.10 is based on the NMR in Appendix 5.5.2, which shows that with an increase of extracted metal ions the amount of lidocaine relative to the amount of decanoic acid in the aqueous phase becomes higher, indicating that indeed an ion exchange mechanism occurs. A small amount of decanoic acid will always dissolve in the water phase, in spite of its limited water solubility. This amount does not increase with an increase in the amount of metal ions that are extracted, which explains the relatively high amount of decanoic acid compared to lidocaine for the extraction of $0.5\,\mathrm{g \cdot L^{-1}}$ $\mathrm{Co^{2+}}$.

Table 5.10: Mole ratio of Lid:DecA for all the water phases measured.

Water phase after extraction of	Molar ratio of Lid:DecA
$0.5\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (2:1)	1:0.34
$0.5\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (3:1)	1:0.26
$0.5\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (4:1)	1:0.19
$2.0\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (2:1)	1:0.05
$2.0\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (3:1)	1:0.02
$2.0\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (4:1)	1:0.03
$4.0\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (2:1)	1:0.01
$4.0\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (3:1)	1:0.01
$4.0\,\mathrm{g\,L^{-1}}$ $\mathrm{Co^{2+}}$ with DecA:Lid (4:1)	1:0.00

5.3.5 Variation of DES/water mass ratios

ϕ_{DES}, which is defined as the DES/water mass ratio, is varied in order to examine its influence on the D of $\mathrm{Co^{2+}}$ (Figure 5.6). The results show that even for low ϕ_{DES} ($\phi_{\mathrm{DES}} < 0.1$), D values of 0.796 and higher can be achieved. The molar ratios of the DecA:Lid induce significant changes especially for the lower mass ratios. It was anticipated that this is caused by a change of hydrophobicity over an increase of the molar ratio of DecA:Lid.

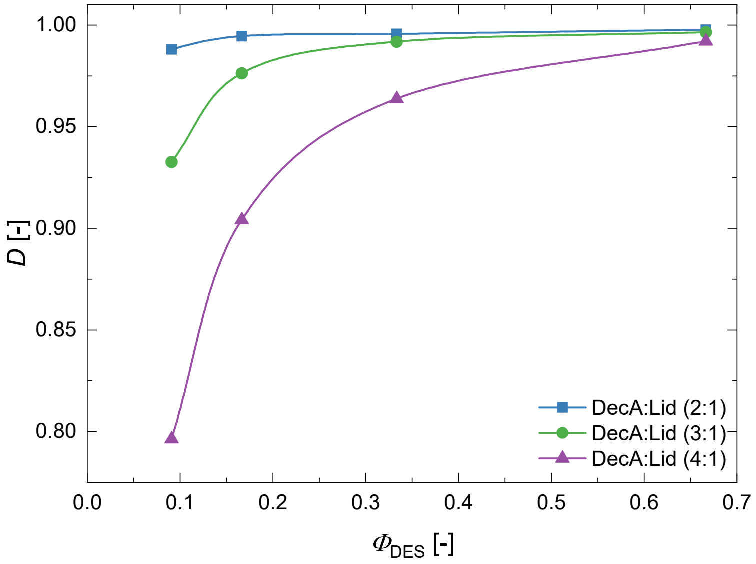


Figure 5.6: Distribution coefficient (D) over different DES/water mass ratios (ϕ_{DES}). The lines are added for clarification purposes.

5.3.6 Variation of extraction time

Moreover, it was found that high D for Co^{2+} as reported here could be achieved within 10 s for all the 3 DES ratios as shown in Figure 5.7.

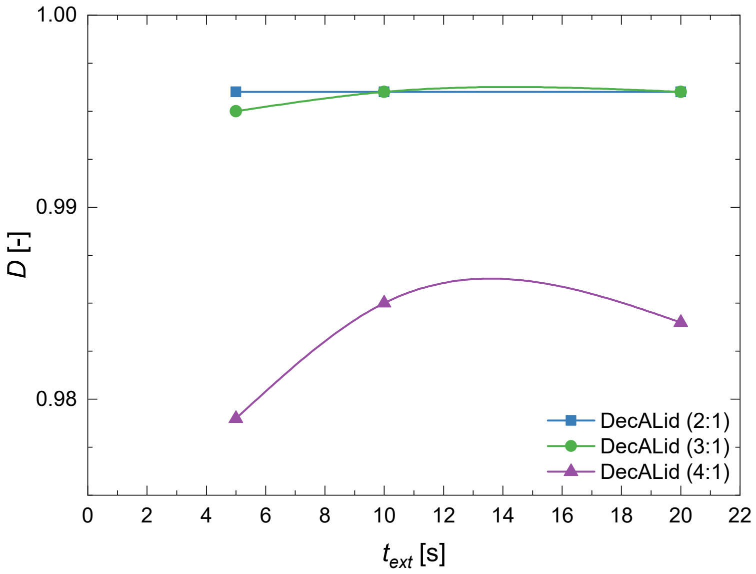


Figure 5.7: Distribution coefficient (D) over a variation of extraction time (t_{ext}). The curves are added for clarification purposes.

5.3.7 Regeneration of the DES

Finally, it was investigated whether regeneration of the DES could be achieved. Sodium oxalate (0.1 M $Na_2C_2O_4$) was used for the regeneration of the DES, since previous research into ILs showed that this was an efficient stripping solution.[134,135] This solution was shaken with an equal mass ratio of DES for 1 h. Analysis of the water phase shows that *D* becomes approximately 0.85–0.90 for the regeneration of Co^{2+} into the water phase (see also Table 5.11). After regeneration with the DES, it was verified whether Co^{2+} extraction from the water phase was still feasible, even though the DES cannot be reused infinitely due to leakage to the water phase. The results show that for the 3:1 and 4:1 ratios of decanoic acid to lidocaine extraction was still possible with high *D*. It is noted that the water phase now became turbid after extraction, even after centrifugation. The most plausible explanation for this is a slight increase in the density of the DES. For the 2:1 ratio of decanoic acid to lidocaine the *D* was only 0.706 after regeneration and it is noted that the volume of the DES phase decreased for the extraction after regeneration.

Table 5.11: Distribution coefficients (*D*) for the extraction and regeneration of Co^{2+} for the DESs.

		DecA:Lid (2:1)	DecA:Lid (3:1)	DecA:Lid (4:1)
Extraction	Co^{2+}	> 0.996	> 0.996	0.983
Regeneration	Co^{2+}	0.848	0.867	0.899
Extraction after regeneration	Co^{2+}	0.706	0.994	0.995

5.3.8 Comparison to ther Solvents

The ability of the hydrophobic DESs to extract metal ions is comparable with ILs based on fatty acids and quaternary ammonium salts.[10,106] Experiments without pH control of the water phase showed metal ion extraction lower than in our case, while they extracted more chloride ions.[10] This can be explained by the difference in the extraction mechanism, which is full metal salt extraction in the case of the ILs.[136] When for ILs the pH of the water phase is adjusted, similar metal ion removal could be achieved as with the DESs.[106]

5.4 Conclusions

In this chapter it was demonstrated that hydrophobic DESs can be used for the removal of metal ions from a non-buffered aquatic environment. All transition metal ions could be removed with high distribution coefficients, as well in a pure metal salt solution as in a mixed metal salt solution. Even at low mass fractions of DES, distribution coefficients for Co^{2+} were close to unity.

An ion exchange process occurs, in which the positively charged metal ion is most likely exchanged with the partially positively charged lidocaine. This claim is supported by an increase of the TOC value upon increasing the metal salt concentration and NMR spectra of the water phase after mixing. These analyses show that only small amounts of decanoic acid were present in the water phase after extraction. Moreover, the concentration of lidocaine in the water phase increases over an increasing starting concentration of Co^{2+}. A time experiment shows that within 10 s the same distribution coefficient can be achieved as after shaking for 1 h. Finally, it was proven that regeneration with a $Na_2C_2O_4$ solution is possible. However, efficient reuse is only possible for the DES with a higher decanoic to lidocaine ratio (3:1 and 4:1).

Overall, the results show the potential of the use of hydrophobic DESs for the removal of metal ions from water. Further research can be directed into two routes. One route can aim at finding other cheaper and greener constituents that can act as ion exchange constituents. Probably, the most preferable route is finding a constituent that is able to be protonated without becoming hydrophilic when taking up a chloride anion and so conduct a complete metal salt extraction.

5.5 Appendix

5.5.1 NMR spectra of the DESs after preparation

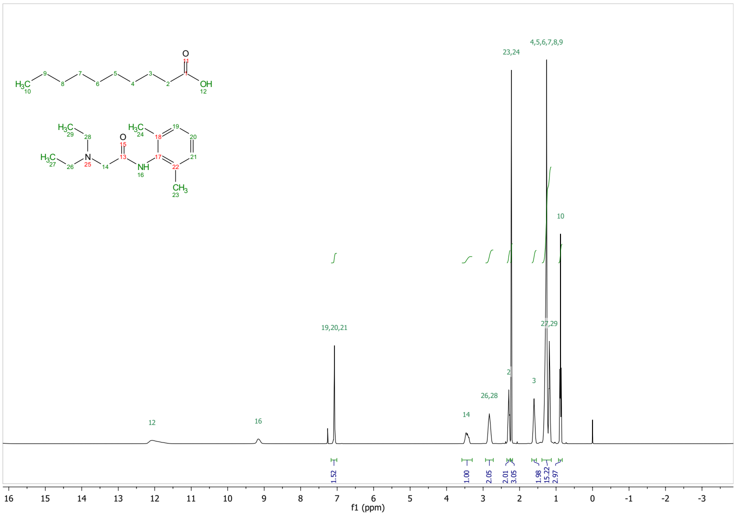


Figure 5.8: ^{1}H NMR of the DES DecA:Lid in a 2:1 molar ratio.

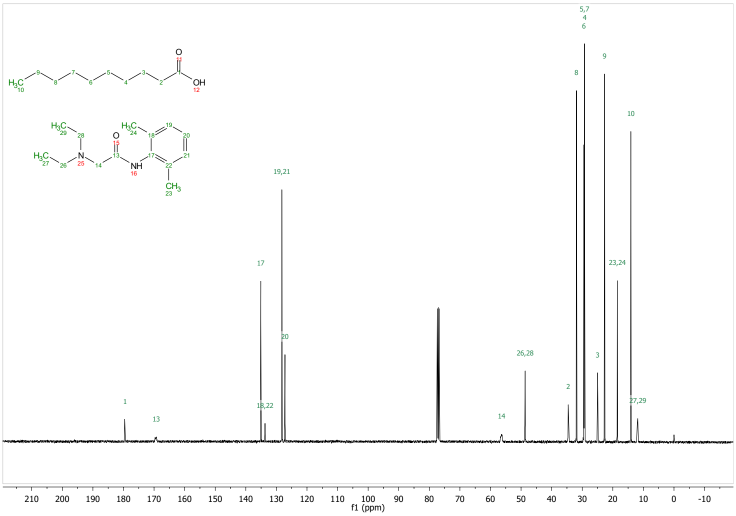


Figure 5.9: ^{13}C NMR of the DES DecA:Lid in a 2:1 molar ratio.

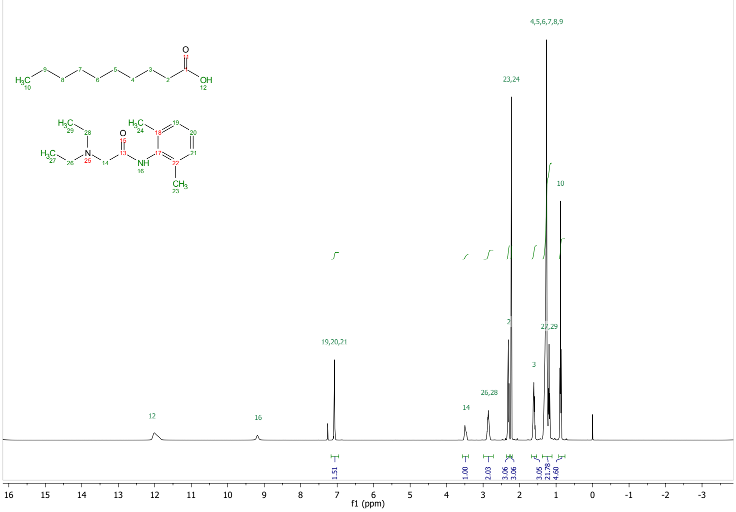


Figure 5.10: ^{1}H NMR of the DES DecA:Lid in a 3:1 molar ratio.

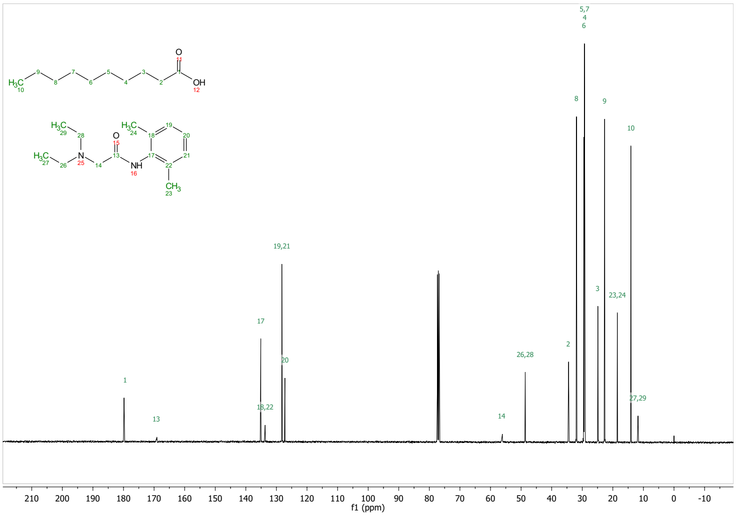


Figure 5.11: ^{13}C NMR of the DES DecA:Lid in a 3:1 molar ratio.

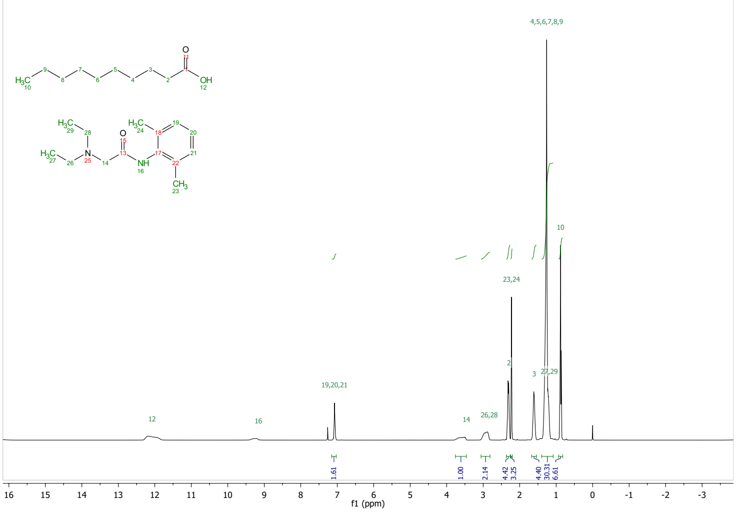


Figure 5.12: ^{1}H NMR of the DES DecA:Lid in a 4:1 molar ratio.

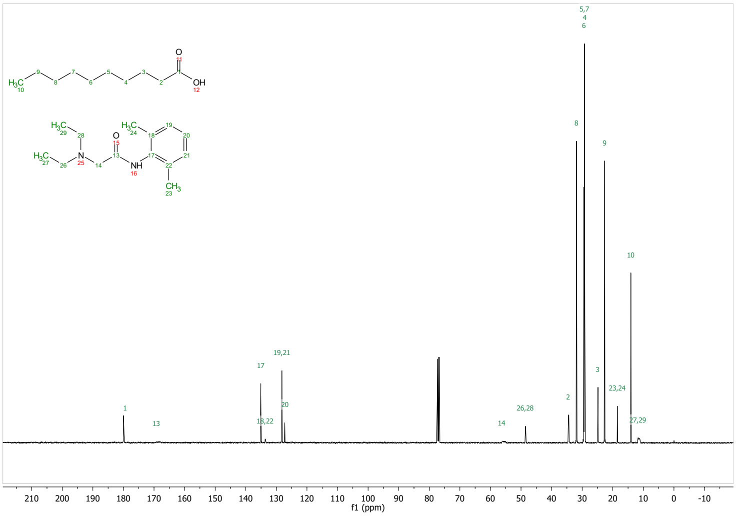


Figure 5.13: ^{13}C NMR of the DES DecA:Lid in a 4:1 molar ratio.

5.5.2 NMRs of the water phases after mixing with the DESs

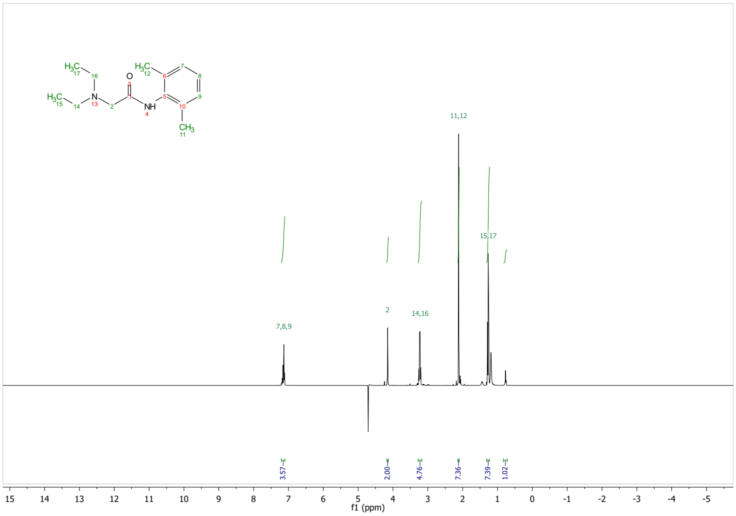


Figure 5.14: NMR spectrum of the water phase (water peak suppressed) after the extraction of $0.5\,\mathrm{g\,L^{-1}}$ Co^{2+} with DecA:Lid (2:1).

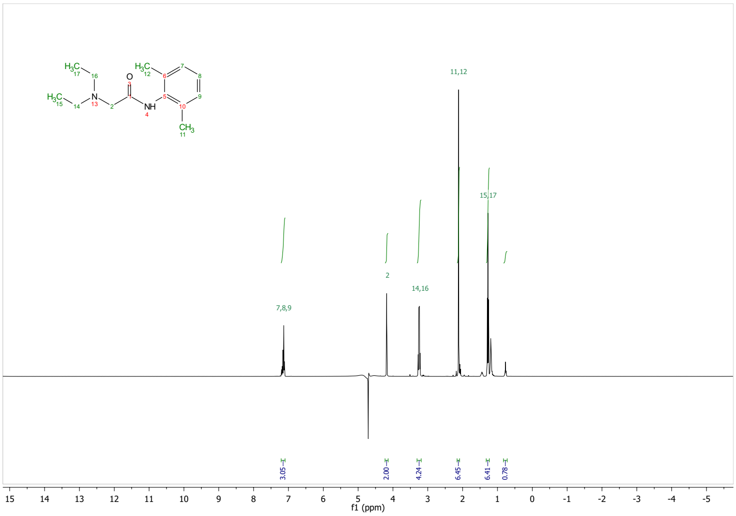


Figure 5.15: NMR spectrum of the water phase (water peak suppressed) after the extraction of $0.5\,\mathrm{g\,L^{-1}}$ Co^{2+} with DecA:Lid (3:1).

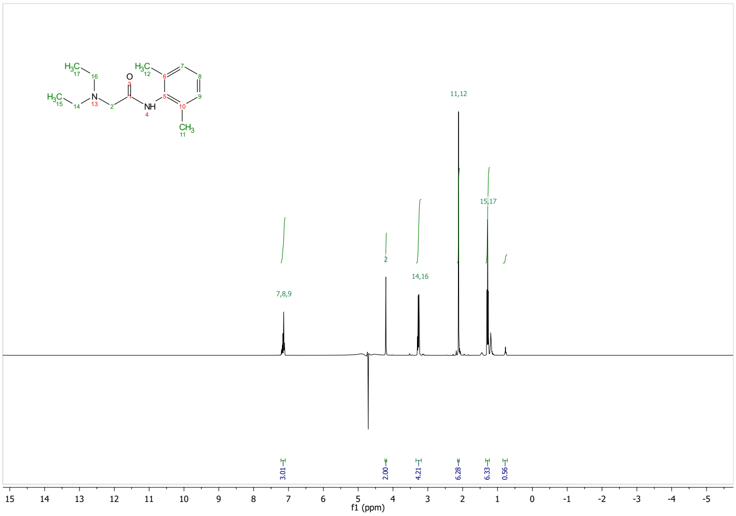


Figure 5.16: NMR spectrum of the water phase (water peak suppressed) after the extraction of 0.5 g L^{-1} Co^{2+} with DecA:Lid (4:1).

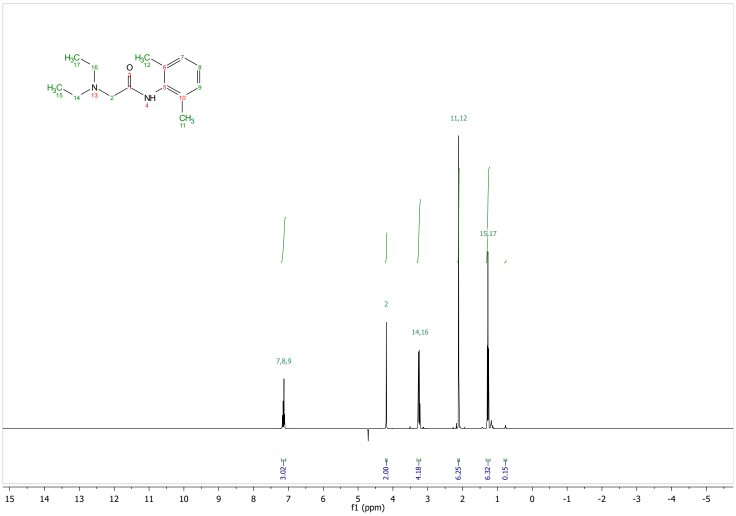


Figure 5.17: NMR spectrum of the water phase (water peak suppressed) after the extraction of 2.0 g L^{-1} Co^{2+} with DecA:Lid (2:1).

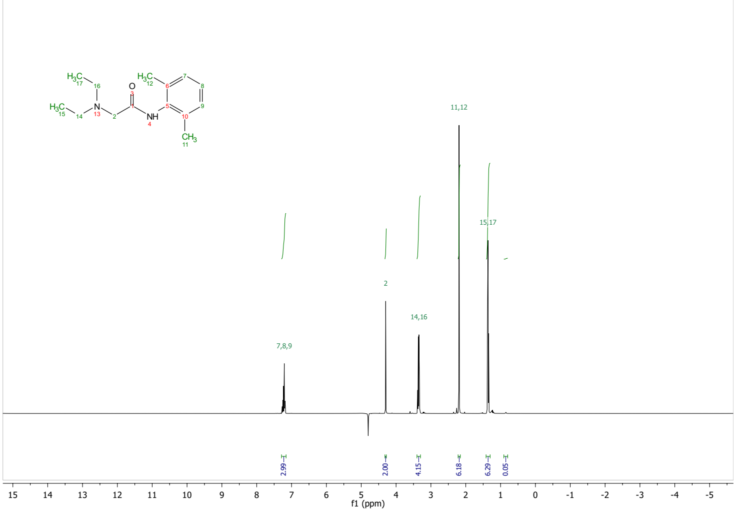


Figure 5.18: NMR spectrum of the water phase (water peak suppressed) after the extraction of 2.0 g L^{-1} Co^{2+} with DecA:Lid (3:1).

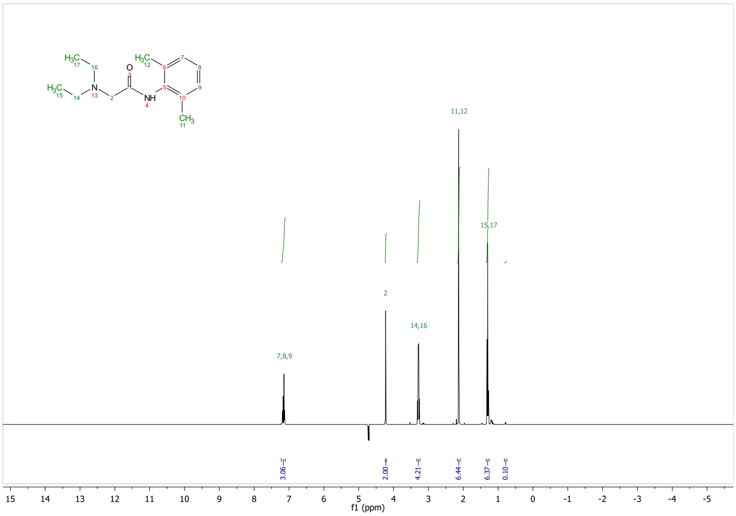


Figure 5.19: NMR spectrum of the water phase (water peak suppressed) after the extraction of 2.0 g L^{-1} Co^{2+} with DecA:Lid (4:1).

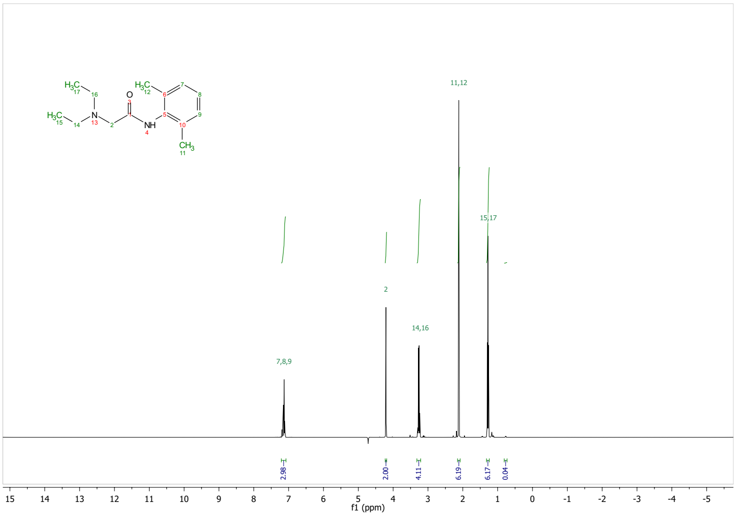


Figure 5.20: NMR spectrum of the water phase (water peak suppressed) after the extraction of 4.0 g L^{-1} Co^{2+} with DecA:Lid (2:1).

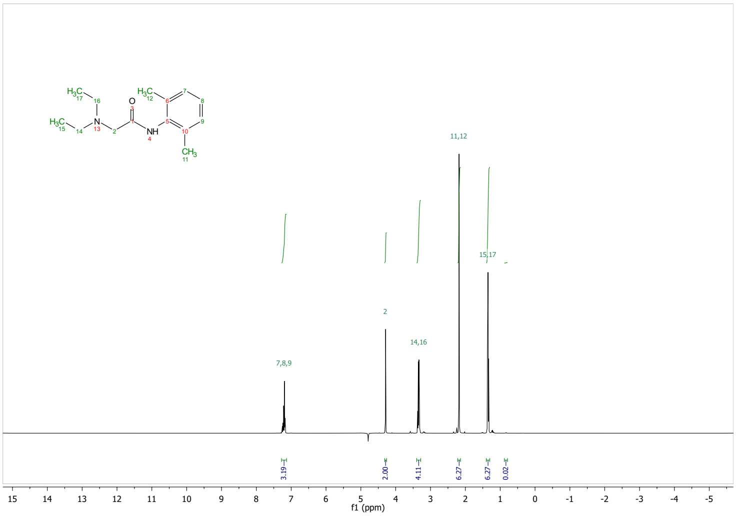


Figure 5.21: NMR spectrum of the water phase (water peak suppressed) after the extraction of 4.0 g L^{-1} Co^{2+} with DecA:Lid (3:1).

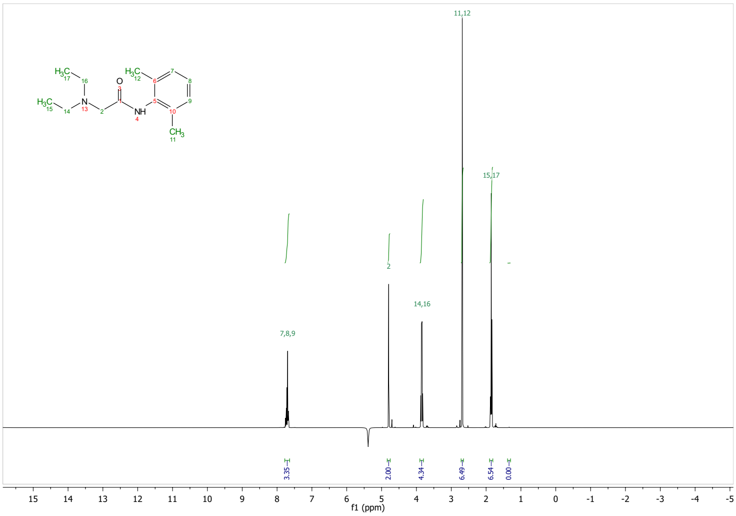


Figure 5.22: NMR spectrum of the water phase (water peak suppressed) after the extraction of 4.0 g L^{-1} Co^{2+} with DecA:Lid (4:1).

Chapter 6

Oil-in-Water Emulsions Prepared with a Hydrophobic Deep Eutectic Solvent

Abstract

Hydrophobic deep eutectic solvents (DESs) are used for the preparation of oil-in-water emulsions. Light microscopy is used to confirm that droplets are formed and zeta potential measurements enable to determine the net charge at the surface of the droplets. The influence on the droplet growth of surfactant concentration, amount of DES, addition of salt and sonication time is investigated with dynamic light scattering. Ostwald ripening of the two-component DES solvent system in water is compared with the single component solvent decane in water. A higher surfactant concentration in the water phase reduces Ostwald ripening, while an increase of the amount of DES leads to an increase of the ripening rate. Moreover, it is shown that sonication times lower than 10 minutes induced a higher Ostwald ripening of the droplets with DES as oil phase. Addition of KCl and NaCl to the aqueous phase only has minor effect on the Ostwald ripening of the emulsion droplets. The results show that hydrophobic DESs can be used to replace conventional oils for the production of oil-in-water emulsions.

Dannie J.G.P. van Osch, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, and Mark Vis, *in preparation*

6.1 Introduction

An emulsion is a liquid-liquid two phase system of droplets of a dispersed phase in a continuous phase that are stabilized by an emulsifier.[137] Examples of emulsifiers include surfactants,[138] polymers and colloids such as silica,[139] and magnetite particles. Emulsions can be divided into three categories, namely microemulsions, nanoemulsions and macroemulsions. Microemulsions form spontaneously and are considered to be thermodynamically stable emulsions, with a diameter of approximately 10-100 nm.[140] Macroemulsions are emulsions with droplet sizes that vary from 1 to 100 µm, which are, at best, kinetically stable and not thermodynamically stable.[141] Nanoemulsions are a class of emulsions between macroemulsions and microemulsions with a droplet size of 0.1-1 µm.[141] They are kinetically more stable than macroemulsions, due to the higher amount of energy that is used to disperse the droplets in the other phase.

In 2003 Binks *et al.*[142] reported emulsions prepared with ionic liquids (ILs) and investigated both IL-in-H_2O as well as H_2O-in-IL emulsions with 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) as oil and silica particles as emulsifier. Previously, emulsions were also prepared from a deep eutectic solvent (DES). Cyclohexane was stabilized with sodium dodecyl sulfate (SDS) to form an emulsion in the hydrophilic DES reline, which is the combination of urea and choline chloride in a 2:1 molar ratio.[143] The major advantage of using these solvents is the fact that they are considered more sustainable than conventional solvents.

In the previous chapters multiple hydrophobic DESs were presented, which were used for the extraction of volatile fatty acids and metal ions from water.[95,96] Furthermore, it has been shown in Chapter 4 that hydrophobic DESs are capable of capturing CO_2.[81,98] The literature shows that hydrophobic DESs can also be used for other applications such as the removal of furfural and hydroxymethylfurfural from water,[97] liquid-liquid microextractions,[83] and the selective removal of extracts from plants.[84,85] An unexplored field with hydrophobic DESs is their use for the formation of oil-in-H_2O emulsions, while this could extend the range of possible applications. Thus, the goal of this chapter is the exploration of hydrophobic DES-in-H_2O emulsions.

Since a DES is composed of two components it was interesting to investigate whether the two-component nature of a DES affects the properties of such emulsions. In this Chapter it is studied whether Ostwald-ripening theory can also describe the emulsion droplet size in case of a DES.

Here, the first results on oil-in-H_2O emulsions with a hydrophobic DES as oil phase are presented. The effects of surfactant concentration, mass fraction of oil (DES) droplets, the addition of salt and sonication time on the droplet size evolution are studied. The hydrophobic DES composed of 1-tetradecanol and menthol in a 1:2 ratio, see Chapter 3, is used for the production of these emulsions. This DES is chosen since it is composed of natural products and satisfies all the criteria set in Chapter 3. The minimum amount of SDS needed to cover the entire DES-water interface is estimated to prevent coalescence of oil droplets in the emulsions. These calculations are based on decane as oil since the necessary data on the hydrophobic DES consisting of 1-tetradecanol (1-tdc) and menthol (Men) in a 1:2 molar ratio was not available. The Lifshitz–Slyozov–Wagner (LSW) theory was used to quantify the Ostwald ripening of the hydrophobic DES in H_2O emulsions.

6.2 Theory

6.2.1 Calculation of the minimum concentration of surfactant to stabilize oil droplets

To avoid coalescence of oil droplets in the emulsion, the minimum amount of surfactant needed to stabilize was estimated as follows. We consider an emulsion of N_d droplets in a volume V. The volume fraction of droplets is

$$\phi_\mathrm{d} = \frac{V_\mathrm{T}}{V}. \tag{6.1}$$

The total surface area of oil droplets reads

$$A_\mathrm{T} = \pi \cdot d^2 \cdot N_\mathrm{d}, \tag{6.2}$$

where, A_T is the total surface area , d is the diameter of the droplets and N_d is the number of droplets present in the emulsion. The total volume of droplets (V_T) can be calculated from:

$$V_\mathrm{T} = N_\mathrm{d} \cdot \frac{\pi}{6} \cdot d^3 \tag{6.3}$$

It follows that the minimum concentration needed to cover the surface area of all oil droplets can be calculated from:

$$C_\mathrm{surf} = \frac{m_\mathrm{surf}}{V} = \frac{6 \cdot \Gamma \cdot \phi_\mathrm{d}}{d}, \tag{6.4}$$

where, C_surf is the overall molar concentration of the surfactant needed to cover all surfaces of the oil droplets. The quantity m_surf is the number of moles of the surfactant on the surface and Γ is the adsorbed amounts of SDS. It is stated in the literature that the area of an SDS molecule at the decane-water interface is approximately $\frac{1}{49 \times 10^{-20}}$ molecules/m^2 for SDS.[144] Hence, it follows from Equation (6.4) that for a mass fraction of decane of 10^{-3} and a droplet diameter of 160 nm a mininum concentration of 0.18 mM should be present in the water phase after dilution. This is in comparison with the concentrations calculated in the literature.[145] The area of an SDS molecule for the DES 1-tdc:Men(1:2) is not known, but it is estimated that is it similar to the one of decane.

6.2.2 Lifshitz–Slyozov–Wagner theory

The growth of droplets in case of Ostwald ripening can be described using the Lifshitz–Slyozov–Wagner (LSW) theory.[146] By assuming steady state kinetics the change of the droplet volume in time follows as:[137,146]

$$\omega = \frac{\mathrm{d}\left(d^3\right)}{\mathrm{d}t} = \frac{8DC_{\mathrm{sat},\infty}\gamma M}{9\rho^2 RT} \tag{6.5}$$

In this equation ω is the rate of Ostwald ripening in $[\mathrm{m}^3 \cdot \mathrm{s}^{-1}]$, t is the time in [s], D is the diffusion coefficient of the dispersed phase in the continuous phase in $[\mathrm{m}^2 \cdot \mathrm{s}^{-1}]$, $C_{\mathrm{sat},\infty}$ is the solubility of the dispersed phase in the continuous phase in $[\mathrm{kg} \cdot \mathrm{m}^{-3}]$, γ is the oil-water interfacial tension $[\mathrm{N} \cdot \mathrm{m}^{-1}]$, M is the molar mass of the disperse phase $[\mathrm{kg} \cdot \mathrm{mol}^{-1}]$, ρ is the density of the dispersed phase $[\mathrm{kg} \cdot \mathrm{m}^{-3}]$, R is the universal gas constant $[\mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}]$ and T is the temperature in [K].

Integration of 6.5 gives:

$$d^3 = d_0^3 + \frac{8DC_{\mathrm{sat},\infty}\gamma M}{9\rho^2 RT} t \tag{6.6}$$

Despite the fact that this theory is confirmed experimentally, in most cases the experimental growth rates are higher then the theoretical ones.[137] Moreover, it should be noted that the samples should be in a dilute solution to apply the LSW theory, which was achieved here by diluting our samples with a factor of 10 upon preparation.

6.3 Experimental section

6.3.1 Materials and preparation

6.3.2 Materials

1-tetradecanol, menthol, sodium dodecyl sulfate, decane, rhodamine B, KCl and NaCl was purchased from Sigma-Aldrich with purities of $\geq$ 97% , $\geq$ 99% and $\geq$ 98.5%, $\geq$ 99%, $\geq$ 95%, $\geq$ 99.0% and $\geq$ 99.5%, respectively.

Preparation of the DES

The DES composed of 1-tetradecanol and menthol in a 1:2 molar ratio was prepared on a 5 gram and a 100 gram scale. A Mettler Ax205 balance was used for weighing the chemicals. 1-tetradecanol was directly added to the glass vial or jar, while menthol was first proportioned in a weighing boat. The amount of menthol was transferred to the 1-tetradecanol phase, after which the solids were properly mixed with a VWR Analog Vortex Mixer. Finally, the DES was stirred until all the solids were transformed into a liquid. The solids that were stuck on the wall were rinsed with the DES in the glassware, after which the DES was stirred until all the solids became part of the liquid. An IKA RCT basic was used for monitoring the stirring speed and temperature. An IKA ETS-D5 temperature controller with an uncertainty of ± 0.1 K was used for temperature control.

Mixing with water

The DES 1-tdc:Men (1:2) was mixed with water to investigate the amount of water it would uptake. Centrifuge tubes (CELLSTAR®) of 50 mL were used, in which 15 grams of water and 15 grams of DES was added. The mixture was vigorously stirred with a vortex mixer for 120 minutes on a IKA KS 4000 I incubating shaker (500 RPM, RT) and afterwards placed in the centrifuge (Sigma 2-16 KL) for 10 min at 6000 rpm. The phases were separated and the DES phase was further analyzed for its water content, density and viscosity.

Preparation of the emulsions

To prepare the emulsions, first stock solutions of 2 and 5 mM sodium dodecyl sulphate (SDS), with or without salt (NaCl of KCl), were prepared with milliQ water. MilliQ water was obtained from a Millipore Milli-Q® biocel, which used a Q-grade® column The weights of the solutions were determined on a Mettler Ax205 balance. An amount of 10 grams of the 2 or 5 mM SDS solution was added to a vial and the corresponding mass fractions of DES oil (m_{oil}) from 1.0×10^{-2} to 2.5×10^{-2} were added to the vial. The aqueous solution and DES phase were mixed on a VWR Analog Vortex Mixer, after which the dispersion was sonicated for 5, 10 or 15 minutes with a Vibra-CellTM ultrasonic liquid processor of the type VCX 130. An amplitude of 80% was used and alternation of 10 seconds occurred between sonicating and not sonicating to avoid excessive heating. Moreover, the vial was placed in an ice bath to surpress heating.

Dilutions of the emulsions for measurements with DLS

The emulsions were diluted with milliQ water. For determination of the size of the droplets, the samples were diluted 10 times to end up with mass fractions, (m_{oil}) or (m_{DES}), ranging from 1.0×10^{-3} to 2.5×10^{-3} and C_{SDS} ranging from 0.2 mM to 0.5 mM. For the zeta-potentials a dilution factor of 50 was used to prevent effects of many body double layer interactions, which resulted in mass fractions, (m_{oil}) or (m_{DES}) of 2.0×10^{-4} and C_{SDS} ranging from 0.04 mM to 0.1 mM.

6.3.3 Analytical methodologies

Water content

Water contents were measured with a Mettler Toledo DL39 coulometer. As titer, 20 v% chloroform with 80 v% Hydranal Coulomat AG was used. Before measuring the samples, the accuracy of the apparatus was checked with water standards of 0.01, 0.1 and 1.0%.

Density/viscosity measurements

The density of the DES 1-tdc:Men (1:2) was measured with an Anton-Paar DMA 4500 M. The density meter has a temperature variation of $\pm$ 0.05 K and an accuracy of the density of $\pm$ 0.05 $\text{kg} \cdot \text{m}^{-3}$. Reference oils were used to measure the discrepancy of the density, which was not more than $\pm$ 0.01 $\text{kg} \cdot \text{m}^{-3}$.

An Anton Paar Lovis 2000 ME rolling ball viscometer was used for measuring the viscosity. A glass capillary with an inner diameter of 1.8 mm was used. This capillary was equipped with a golden ball. The maximum coefficient of variation was below 0.2%, while the forward/backforward deviation was less than 1.0%. A N26 calibration oil supplied by Anton-Paar was used for calibration of the capillary.

Dynamic light scattering measurements

Dynamic light scattering (DLS) measurements were performed with a Malvern Zetasizer under an angle of 173° to measure the z-average hydrodynamic diameter of the oil-in-water emulsion droplets. A point in the graphs responds to 20 measurements of 20 seconds. All systems where prepared and measured for at least two times, which represents the standard deviations in the graph.

Microscopy

Samples were dyed using rhodamine B for observation using fluorescence microscopy on a Nikon Eclipse Ti-E inverted microscope. A spatially point of rhodamine B was added after preparation of the emulsions. This microscope was equipped with a Nikon CFI Apo TIRF objective (100x magnification, N.A. 1.49), Hamamatsu ORCA-Flash4.0 V2 camera, Nikon Intensilight C-HGFl mercury lamp and a Semrock TRITC-B fluorescence filter.

Surface tension measurements

Surface tension measurements were performed with a Krüss K11 MK4 tensiometer via the Wilhelmy plate method. A Wilhelmy plate from platinum with dimension of 19.9x0.2x10 mm (WxDxH) was used. The tensiometer has a measuring range between 1 and 999 $\mathrm{mN} \cdot \mathrm{m}^{-1}$ and a temperature range of 263.15 to 403.15 K. The resolution is $0.1\,\mathrm{mN} \cdot \mathrm{m}^{-1}$, while it has a standard deviation of $0.03\,\mathrm{mN} \cdot \mathrm{m}^{-1}$.

For the surface tensions three consecutive measurements were performed. After each measurement the Wilhelmy plate was burned with a Bunsen burner to remove the DES and placed back. Before a new measurement, the system is equilibrated for at least 15 minutes. All samples were stirred properly to enhance equilibration.

6.4 Results and discussion

6.4.1 Physicochemical properties

In Chapter 3 a vast amount of the physicochemical properties of the DES composed of 1-tetradecanol and menthol in a 1:2 molar ratio was reported. The degradation temperature of this DES is 113.1 ± 8.4 °C. Before mixing with water, the density at 20 °C is $872.1\,\text{kg}\cdot\text{m}^{-3}$, while after mixing with water the density is $874.2\,\text{kg}\cdot\text{m}^{-3}$. Here, the density is investigated as function of temperature to get some detailed insights. The correlation between the densities and temperature is found to be linear:

$$\rho = a + bT \tag{6.7}$$

Table 6.1: Fitting parameters for the density as depicted in equation 6.7.

DES	a [$\text{kg}\cdot\text{m}^{-3}$]	b [$\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$]
Before mixing with water	1081.44	-0.71
After mixing with water	1085.31	-0.72

As shown in Figure 6.1 this expression accurately describes the measured densities of the DES before and after mixing with water. The fit parameters a and b are presented in Table 6.1.

We describe the viscosity using the Vogel-Fulcher Tamman (VFT) expression:

$$\eta = A_\eta \cdot \exp \frac{B_\eta}{T - C_\eta} \tag{6.8}$$

The change in viscosity of the DES before and after mixing with water is given in Figure 6.2. The fit parameters for the VFT equation are given in Table 6.2.

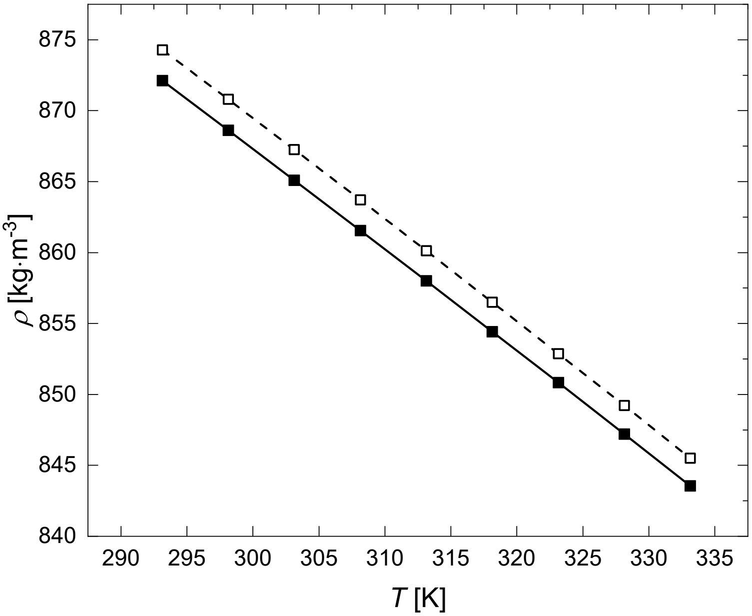


Figure 6.1: Temperature dependence for the density of 1-tdc:Men (1:2) before (closed symbols) and after (open symbols) mixing with water. The water content before mixing (closed symbols) is 289.0 ± 1.0 ppm, while after mixing (open symbols), this is 1.77 ± 0.01 wt%.

Table 6.2: Fitting parameters of the Vogel-Fulcher-Tammann (Equation 6.8).

DES	A_η [mPa · s]	B_η [K]	C_η [K]
Before mixing with water	9.797×10^{-3}	1025.63	-171.30
After mixing with water	3.854×10^{-2}	715.51	-188.27

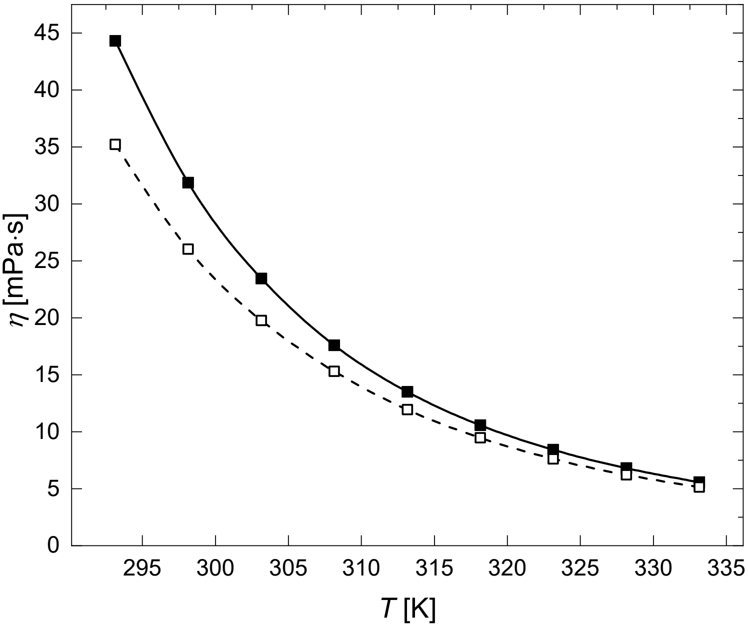


Figure 6.2: Viscosity as a function of temperature for 1-tdc:Men (1:2) before (closed symbols) and after (open symbols) mixing with water. The water content before mixing is 289.0 ± 1.0 ppm, while after mixing it is 1.77 ± 0.01 wt%.

Another physicochemical property of the DES 1-tdc:Men (1:2) that was investigated is the surface tension between DES and air. The surface tension gives indirect information on the intermolecular forces within the liquid. The surface tension for the DES at 293.15 K is $29.33 \pm 0.06\ \mathrm{mN \cdot m^{-1}}$. This is slightly higher than decane, which has a surface tension of $24.47 \pm 0.06\ \mathrm{mN \cdot m^{-1}}$,[147] but also somewhat higher than most organic solvents. Most likely, the DES 1-tdc:Men (1:2) has stronger intermolecular attractions, such as hydrogen bonding between the alcohol groups, which induces the higher surface tension.

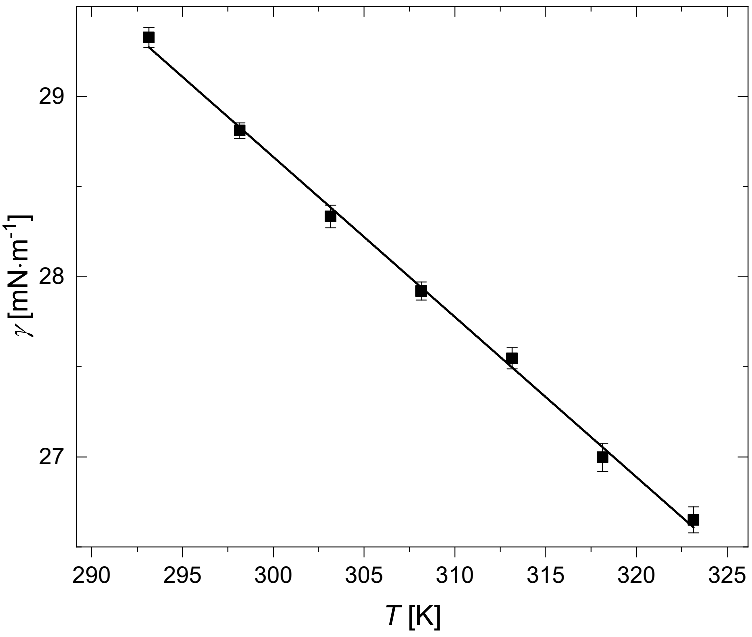


Figure 6.3: Temperature dependence of the air-DES surface tension with the fit $\gamma = \alpha T + \beta$.

In Figure 6.3 we plot the temperature dependence of the surface tension. This enables to calculate the surface entropy, $S^\sigma = -\mathrm{d}\gamma/\mathrm{d}T$, which gives more information on the orientation of the surface. For the DES 1-tdc:Men (1:2) $\mathrm{d}\gamma/\mathrm{d}T$ was found to be $-0.089\,\mathrm{mN\,m^{-1}\,K^{-1}}$. In literature for the hydrophobic solvents decane and hexadecane surface entropies of -0.094 and -0.091 $\mathrm{mN\,m^{-1}\,K^{-1}}$, respectively, were found.[147] Thus, the surface entropy of the DES 1-tdc:Men (1:2) matches to the one of these two conventional solvents.

6.4.2 Microscopy

Before measuring the time evolution of the droplet size with DLS, light microscopy was used to confirm that droplets are formed, and not particles with anisotropic shapes. Figure 6.4 shows a representative microscopy image that confirms that droplets are formed after dispersing DES into water.

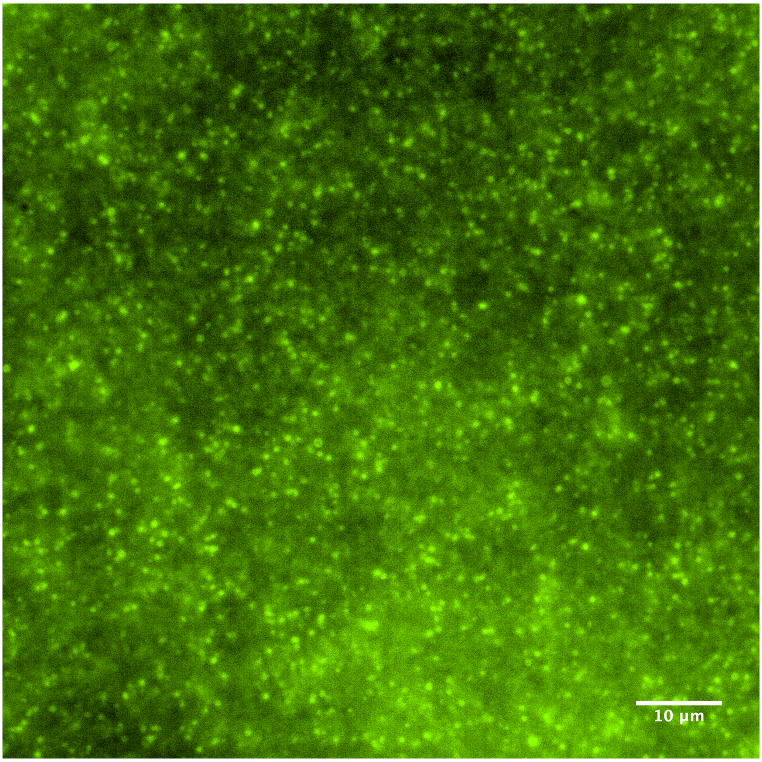
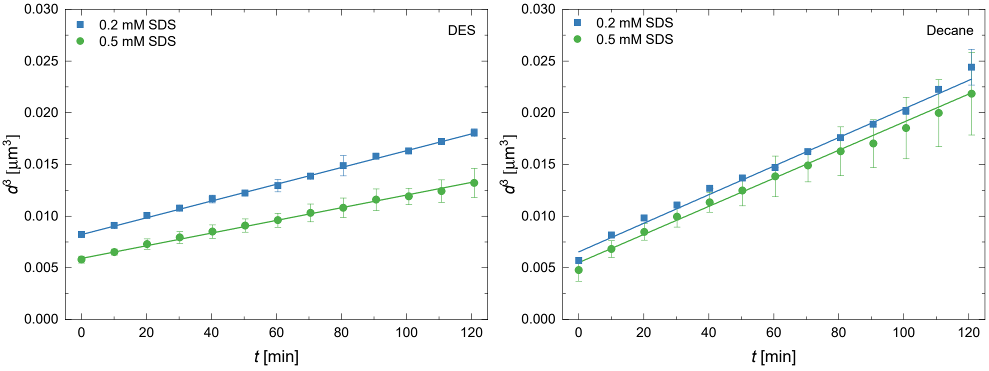


Figure 6.4: Light microscopy image of the emulsion droplets. The bar indicates the length scale. The droplets were labeled with Rhodamine B. The concentrations of SDS in H_2O used after dilution with a factor 10 are, 0.5 mM and the mass fraction m_{oil} was 1×10^{-3}.

6.4.3 Influence SDS concentration on the droplet growth

DLS measurements are performed over the first two hours after preparation of the DES-in-H_2O emulsions to investigate the growth of droplets over time. The measured diffusion coefficients were converted to z-averaged hydrodynamic diameters using the Stokes-Einstein equation. The resulting hydrodynamic diameter for emulsions prepared with decane and DES are plotted in Figure 6.5, where the effect of SDS concentration is illustrated.



(a) **(b)**

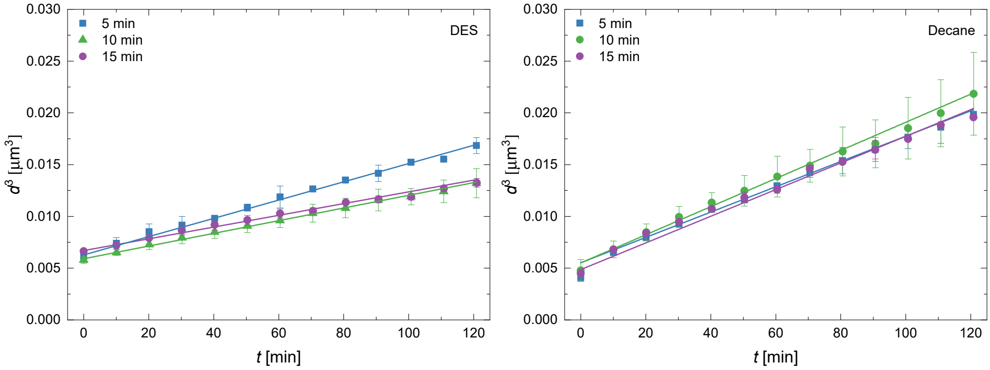
Figure 6.5: Time evolution of the average droplet volume calculated expressed as d^3 from the z-average diameter obtained via DLS. In Figure 6.5a the DES 1-tdc:Men (1:2) is used as oil phase, while in Figure 6.5b decane is the oil phase. The concentrations of SDS in H_2O used after dilution with a factor 10 are, 0.2 and 0.5 mM and for all experiments the mass fraction m_{oil} was 1×10^{-3}.

The LSW theory predicts that the droplet growth scales as $d \sim t^{\frac{1}{3}}$, so all experimental data was fitted to $d = q \cdot t^{\frac{1}{3}} + d_0$ where q is $\frac{8DC_{\text{sat},\infty}\gamma M}{9\rho^2 RT}$. As expected, for both the DES and decane a steeper growth of the droplets is observed upon a decrease of SDS concentration from 0.5 mM to 0.2 mM. For decane as oil the linear slope is similar for the 0.2 and 0.5 mM SDS, while for DES as oil the slope is slightly higher for the 0.2 mM SDS. It may be that a DES droplet is not completely covered with SDS at these surface concentrations since SDS covers a different area per molecule in comparison to decane. It is also possible that SDS dissolves better into the DES, so fewer DES is available at the interface. Furthermore, it seems that the DES-in-water emulsions have a lower droplet growth rate in comparison with the decane-in-water emulsions.

As follows from LSW theory three factors that can influence the droplet growth rate are: 1) the oil-water interfacial tension, (2) solubility of the organic phase in the water phase and (3) the diffusion coefficient of the organic phase to the aqueous phase. Calculations of the theoretical droplet ripening rates with the LSW theory are presented in 6.4.8

6.4.4 Influence of sonication on droplet growth

The influence of the sonication time on the droplet growth for both decane-in-water and the DES-in-water emulsions was investigated as shown in Figure 6.6. The conventional solvent decane as oil shows no clear differences in growth rate upon variation of the sonication time. For 10 minutes sonication a steeper slope was detected, but the standard deviation of this measurement is also bigger in comparison with 5 and 15 minutes of sonication. For the DES as oil, 5 minutes sonication time shows a larger slope in comparison with 10 and 15 minutes sonication time. It is assumed that within 5 minutes the solution is not fully emulsified due to the higher viscosity of the 1-tdc:Men (1:2) in comparison to decane. This motivated us to sonicate the dispersion for 10 minutes.



(a) **(b)**

Figure 6.6: Average droplet z-average droplet diameter obtained from DLS measurements over time for different sonication times used, namely 5, 10 and 15 minutes. In the figure on the left, Figure 6.6a, the DES 1-tdc:Men (1:2) is used as oil phase, while in the right figure, Figure 6.6b, decane is the oil phase. Upon dilution with a factor 10, a surfactant concentration of 0.5 mM SDS in water was used, while m_{DES} was 1×10^{-3}.

6.4.5 Influence of DES mass fractions

In Figure 6.7 the effect of mass percentage of the DES phase is plotted, where upon dilution 0.5 mM SDS was present in the aqueous phase. The evolution of the droplet size is quite similar for $m_{\mathrm{DES}} = 1 \times 10^{-3}$ and 1.5×10^{-3}. It is hypothesized that at these low mass fractions of DES a dilute solution is made, in which the LSW theory is applicable. Similar mass fractions were also applied in the literature for decane, which verifies our hypothesis.[145] The growth rate of the droplets increase with the amount of DES in the water phase above $m_{\mathrm{DES}} = 1.5 \times 10^{-3}$, which is most likely caused since the system is not a dilute one anymore.

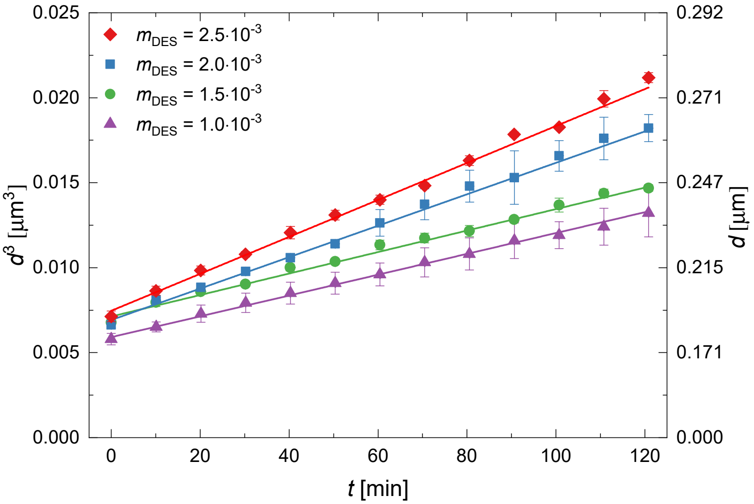
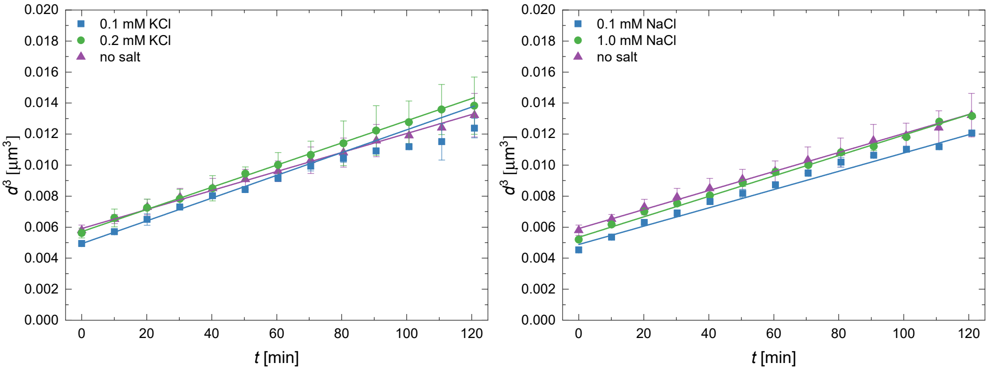


Figure 6.7: Time evolution of the average droplet volume calculated expressed as d^3 from the z-average diameter for different mass fractions m_{DES} of 1-tdc:Men(1:2) as oil phase. A concentration after dilution of 0.5 mM of SDS in water was used as concentration.

6.4.6 Influence salt addition on the droplet growth

Furthermore, the addition of different salt concentrations was investigated. Figure 6.8 illustrates the effect of the different salt concentrations on the droplet growth. It is clear that there is no perceptive influence on salt concentration. The differences fall within the reproducibility margins of the two to three different experiments.



(a) **(b)**

Figure 6.8: Influence of salt concentration on the average droplet z-average diameter obtained via DLS. A surfactant concentration after dilution of 0.5 mM SDS in water was used, while m_{DES} was 1×10^{-3}. For KCl, Figure 6.8a, concentrations of 0.1 and 0.2 mM were present in the water phase upon dilution, while for NaCl, Figure 6.8b, the concentrations were 0.1 and 1 mM, compared to the experiments in absence of salt.

6.4.7 Zeta-potentials

The zeta-potentials at the droplet surfaces in the different emulsions were measured to investigate the sign and magnitude of the surface charge of the droplets (Table 6.3). The results show that all the prepared emulsions are negatively charged, which may be expected due to the negatively charged SDS surfactant at the oil-water interface. Most of the emulsions we prepared have a zetapotential close to -60 mV. Emulsions prepared with 0.04 mM SDS solution or with the addition of 0.02 mM KCl contain droplets with slightly larger zeta potentials. It is hypothesized that for the latter cases the SDS coverage of the droplets is slightly lower, which leads to a lower zeta-potential.

Table 6.3: Zeta-potentials of emulsions measured after dilution with a factor 50, $m_{\text{oil}} = 2 \times 10^{-4}$.

C_{SDS} (after dilution) [mM]	Oil phase	Salt addition	Zeta potential [mV]
0.04	1-tdc:Men (1:2)	No	-54.6 ± 0.69
0.1	Decane	No	-58.4 ± 1.96
0.1	1-tdc:Men (1:2)	No	-59.0 ± 0.59
0.1	1-tdc:Men (1:2)	0.02 mM KCl	-53.6 ± 0.98
0.1	1-tdc:Men (1:2)	0.04 mMKCl	-60.2 ± 1.25
0.1	1-tdc:Men (1:2)	0.02 mM NaCl	-59.6 ± 2.89
0.1	1-tdc:Men (1:2)	0.2 mM NaCl	-60.7 ± 0.77

6.4.8 Comparison with the LSW theory

We estimated the ripening rates of emulsion droplets prepared with decane and DES as oil phase based on the growth rates as presented in Figure 6.5 to 6.8. The ripening rates for the decane-in-water emulsions were compared with literature values. As proposed in literature, the growth rate is calculated by dividing the linear correlations presented in Figure 6.5 to Figure 6.8 with $(1.14)^3$ to transform the z-average diameters to number-average diameters.[148,149] These growth rates are presented in Table 6.4.

The growth rates of the emulsions with decane as oil phase are comparable to the experimental results of Soma *et al.*,[145] who also presented results of Ostwald ripening with 0.5 mM solution of decane. They used a volume fraction of 2×10^{-3} decane, which is a mass fraction of approximately 1.46×10^{-3}.[145] This is an approximate value of 1.46 times larger than the oil mass fraction used throughout our investigation, which most likely will have no influence on the growth rate since it is in the diluted region. Despite, their growth rate is approximately 9.5 times smaller. It should be mentioned that they divide their z-average diameter with $8 \cdot (1.14)^3$.[145]

The experimental ripening rates of the emulsions prepared with the hydrophobic DESs are compared to the ripening rates of decane-in-water emulsions. The results show that the ripening rates of the DES-in-water emulsions are lower than the decane-in-water emulsions. Future research should be directed into finding the parameters of the LSW theory so that the theoretical ripening rate can be calculated and a comparison between theoretical and experimental rates can be made.

Table 6.4: Experimental Ostwald ripening rates of the different experiments performed throughout this work.

C_{SDS} [mM]	m_{oil}	Oil phase	Salt addition	ω [$m^3\,s^{-1}$]
0.2	1×10^{-3}	1-tdc:Men (1:2)	No	9.12×10^{-25}
0.2	1×10^{-3}	Decane	No	1.55×10^{-24}
0.5	1×10^{-3}	Decane	No	1.53×10^{-24}
0.5	1×10^{-3}	1-tdc:Men (1:2)	No	6.89×10^{-25}
0.5	1.5×10^{-3}	1-tdc:Men (1:2)	No	7.11×10^{-25}
0.5	1×10^{-3}	1-tdc:Men (1:2)	0.1 mM KCl	8.04×10^{-25}
0.5	1×10^{-3}	1-tdc:Men (1:2)	0.2 mM KCl	8.25×10^{-25}
0.5	1×10^{-3}	1-tdc:Men (1:2)	0.1 mM NaCl	7.41×10^{-25}
0.5	1×10^{-3}	1-tdc:Men (1:2)	1.0 mM NaCl	6.63×10^{-25}

The theoretical ripening rates can be determined with Equation 6.5. The parameters for decane are found in the literature. These parameters are given in Table 6.5 together with the parameters known for the DES. The unknowns for the DES are the diffusion coefficient and the interfacial tension. They were estimated at $5 \times 10^{-10}\ m^2 \cdot s^{-1}$ and $8 \times 10^{-3}\ N \cdot m^{-1}$. Values in the range of hexane to hexadecane.[150]

Table 6.5: Parameters for the LSW theory for decane[150] and 1-tdc:Men (1:2).

Parameters	Decane	1-tdc:Men (1:2)
D [$m^2 \cdot s^{-1}$]	7.15×10^{-10}	5×10^{-10}
$C_{sat,\infty}$ [$kg \cdot m^{-3}$]	5.20×10^{-5}	0.273
γ [$N \cdot m^{-1}$]	8.41×10^{-3}	8×10^{-3}
M [$kg \cdot mol^{-1}$]	142.28×10^{-3}	175.64×10^{-3}
ρ [$kg \cdot m^{-3}$]	727	872

This gives a theoretical growth rate of decane of $3.1 \times 10^{-26}\,\mathrm{m}^3 \cdot \mathrm{s}^{-1}$, while this is $9.2 \times 10^{-20}\,\mathrm{m}^3 \cdot \mathrm{s}^{-1}$ for 1-tdc:Men (1:2). The difference in theoretical and practical growth rate for decane is in the same order as observed in the literature.[149] The difference for the DES is larger than observed in the literature. It is anticipated that the DES behaves differently in an emulsion and so the saturated concentration as measured in Chapter 3 is differently.

6.5 Conclusions

Oil-in-water emulsions prepared with a hydrophobic deep eutectic solvent (DES) were presented. As oil phase it was chosen to use a binary mixture composed of 1-tetradecanol and menthol in a 1:2 molar ratio was used, while the surfactant used to stabilize the emulsion was sodium dodecylsulphate.

We tested whether the DES-based emulsion followed classic Ostwald ripening to verify whether the nature of a two-component solvent such as a DES affects the properties of the emulsion. It can be concluded that Ostwald ripening indeed applies to oil-in-water emulsions prepared with a hydrophobic deep eutectic solvent.

The influence of different SDS concentrations was tested. A higher SDS concentration leads to a lower ripening rate of the droplets. A higher DES mass fraction increases the growth rate of the droplets, while the addition of the salts KCl and NaCl had no influence on the growth rate. It should also be mentioned that for the case of the hydrophobic DES as oil phase a shorter sonication time induced a higher ripening rate of the droplets than in the case of 10 minutes. Further investigation of the ripening rates led to the conclusion that they are similar to those of decane-in-water and of other hydrocarbons, as presented in the literature.

Overall, it can be concluded that DES-in-water emulsions behave similarly as conventional oil-in-water emulsions and the droplet growth can be described by Ostwald ripening. Despite, the LSW theory does not predict the ripening rates accurately. The next step would be the formation of emulsions with a hydrophobic DES as oil phase that avoids Ostwald ripening to form droplets with a stable diameter in the water phase. Since the solubility of the oil phase plays a major role, finding an oil phase with a lower solubility in the water phase could be useful, as well as the addition of an insoluble oil that can prevent Ostwald ripening.

6.6 Acknowledgements

We would like to thank Nicole M.W. van der Heijden for carefully performing many experiments. Moreover, Van ’t Hoff Laboratory for Physical and Colloid Chemistry (UU) is acknowledged for the use of their microscope.

Chapter 7

Summary and Outlook

7.1 Summary

Design and Applications of Hydrophobic Deep Eutectic Solvents

Solvents play a crucial role in the chemical industry. They act as medium for many chemical reactions, enable the application of separation technology such as extractions and membrane separations, but are also key elements in the production of emulsions. A disadvantage of many solvents is their hazardous influence on the environment and the health of human beings. Ideally, these environmentally harmful solvents should be replaced by more sustainable and innovative ones. A group of more sustainable (and innovative) solvents that have been investigated for the replacement of conventional ones are ionic liquids (ILs). These ILs are typically prepared via a chemical reaction and need purification, making them expensive and not preferable for the chemical industry.

In 2003 a new class of innovative solvents, deep eutectic solvents (DESs), were introduced in the literature. DESs have similar physicochemical properties as ILs, but need no purification step since they can be easily prepared by simply mixing the two components of the DES. By avoiding this purification step they are cheaper in comparison to ILs, making them interesting solvents for future use in the chemical industry.

DES research has focused mainly on hydrophilic DESs. This thesis focuses on the investigation, design and application of hydrophobic DESs, a new class of sustainable and innovative hydrophobic solvents. A hydrophobic deep eutectic solvent consists of two hydrophobic solid substances, that form a liquid due to mixing entropy, hydrogen bonding, and/or Van der Waals interactions. In comparison to the melting point of the two pure components, the melting point of the DES should be exceedingly lower. Chapter 1 gives an introduction into (more) sustainable solvents, while Chapter 2 is based on the first reported investigation on the preparation of hydrophobic DESs. These hydrophobic DESs consist of decanoic acid and a variation of quaternary ammonium salts, varying from tetrabutylammonium chloride to tetraoctylammonium bromide. Their physicochemical properties are measured after preparation and compared to those of hydrophilic DESs. The cross-contamination between the DES and water phase is assessed to obtain more information on the amounts of DES that transfers to the water phase and how much water these hydrophobic DESs absorb. To investigate the potential of these new DESs on practical industrial applications they were successfully evaluated for the recovery of volatile fatty acids from diluted aqueous solutions.

In Chapter 3, a thorough study evaluated 507 combinations of solid components based on terpenes, from which 17 systems were classified as new hydrophobic DESs. From these 17 hydrophobic DESs their water content, density and viscosity is measured after preparation. Nuclear magnetic resonance analysis is performed to assess whether the DES remained an unreacted mixture, while thermogravimetric analysis is used to measure the degradation temperature of the developed hydrophobic DESs. Their sustainability and future use for academia and industry is investigated via four main criteria. These criteria include the difference in density with water $\geq 50\,\mathrm{kg\,m^{-3}}$, a viscosity as low as possible ($< 100\ \mathrm{mPa \cdot s}$), a small amount of DES that transfers to the water phase and a pH that remained between 6 and 8. The results show that 5 hydrophobic DESs satisfy these criteria. Finally, a selected group of these DESs are applied for the removal of riboflavin (vitamin B2) from the aquatic environment with moderate to good extraction ability.

In Chapter 4 the hydrophobic DESs composed of decanoic acid and quaternary ammonium salts, as introduced in Chapter 2, are used for the capture of CO_2. The results show that the solubilities of CO_2 in hydrophobic DESs depend on the molar volume of the DES. The higher the molar volume, the higher the solubility of CO_2 in them. Moreover, different cycles of absorption and regeneration show no signs of degradation of the DESs. Henry's law constant is used for comparing the CO_2 solubilities in the DES with conventional solvents and ionic liquids. DESs composed of decanoic acid and the ammonium salts tetraoctylammonium chloride and tetraoctylammonium bromide have a similar CO_2 solubility as the IL ([C_4mim][BF_4]). The solubilities of the hydrophobic DESs could be predicted with the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) model with parameters only fitted to liquid densities. The results show that reasonable to good predictions can be made with this model.

Chapter 5 shows the use of hydrophobic DESs consisting of decanoic acid and lidocaine for the removal of metal ions from water. A 2:1, 3:1 and 4:1 decanoic acid to lidocaine molar ratio of the hydrophobic DESs is investigated. The results show that transition metal ions can be extracted with high efficiency, while for alkali metal ions the extraction efficiency is moderate. In a batch experiment with both transition and alkali metals, the alkali metals are removed from the water phase with low efficiency, while the efficiency remains similar for the hydrophobic DESs. Higher starting concentrations of Co^{2+} and higher DES to H_2O mass ratios still give high efficiencies. A maximum extraction efficiency is achieved within 5 s and it was demonstrated that regeneration was possible. The extraction mechanism is based on ion exchange.

Chapter 6 introduces hydrophobic DES-in-water emulsions. The hydrophobic DES oil phase of the emulsion is 1-tetradecanol+menthol in a 1:2 molar ratio, while the stabilizing surfactant is sodium dodecyl sulphate. Physicochemical properties such as the density, viscosity and surface tension of the DES are measured to characterize the hydrophobic DES. Microscopy is used to show that DES-in-water emulsion droplets are formed. The size and growth of these droplets is analyzed using dynamic light scattering. The evolution of the droplet size can be described using Ostwald ripening. The influence of concentration of sodium dodecyl sulphate, the mass fraction of DES and the addition of salt on the droplet size were tested. An increase of SDS concentration reduces the droplet growth rate. Mass fractions up to 1.5×10^{-3} show similar growth rates due to the fact that a dilute solution is made. The addition of salt to the emulsions has no influence on the droplet growth. Calculations of the droplet ripening rates show similar growth rates as in the literature.

The developed hydrophobic DESs presented in this thesis open up a new field of research for the investigation of water-immiscible solvents. The hydrophobic DESs developed can be considered as sustainable and innovative due to lower viscosities, easier separation of DES and water, lower cross-contamination and the use of natural components. Future research is expected to demonstrate their potential for further use in academic research and whether they are suitable solvents for use in the chemical industry.

7.2 Outlook

In this thesis hydrophobic eutectic solvents and their properties are presented. Further, comprehensive steps towards application are made for these sustainable and innovative hydrophobic DESs. In the following paragraphs an outlook will be presented for future research that may help to realize the next steps in the field of hydrophobic DESs. An important next step in the field of hydrophobic DESs would be fundamental research to understand their formation and the intermolecular interactions that influence this formation. Theoretical insights should be obtained via density functional theory calculations and molecular dynamics simulations, but also more practical work such as the formation of phase diagrams of both the solid-liquid equilibrium and the liquid-gas equilibrium should be considered to obtain more fundamentals and insights in their thermodynamic properties.

Knowledge about the formation of hydrophobic DESs from the two solid components and the future potential applications will accelerate future experimental work. It would be of use to develop models that, with as less as free parameters as possible, can predict the phase behavior of DESs so that without performing experiments it can be predicted whether two components would form a DES. Moreover, models should be developed that predict the requirements and performance of a DES in a certain application. In this thesis a predictive tool is used for the prediction of solubilities of CO_2 in hydrophobic DESs based on decanoic acid and quaternary ammonium salts, but more predictive models should be developed. A combination of such models would give a tool that would save us tremendous amounts of labor work and time.

Throughout this thesis a vast amount of data and results on physicochemical properties of DESs and applications of DESs are obtained, but also knowledge on the formation of hydrophobic DESs. Next to the before mentioned theoretical models that should be developed, it is of importance to investigate many parameters for newly developed hydrophobic DESs after preparation and after mixing with water. Parameters of importance are:

- The water contents, density and viscosity of the hydrophobic DES before and after mixing with water.
- Chemical analyses of the DES phase to investigate whether the components did not undergo a reaction.
- DES phase transferred to the water phase via analytical techniques that give more information on:
  - (i) The pH of the water phase.
  - (ii) The amount of DES components transferred to the water phase (For example by measuring total organic carbon, ion chromotagraphy, nuclear magnetic resonance).

In the case of emulsions also the following parameters should be considered:

- Surface tension of the DES.
- Interfacial tension of the DES phase with water.
- Interfacial tension of the DES phase and water with surfactant.

Despite the fact that it is not investigated in this thesis, it should become standard to also determine biodegradability and toxicity of newly developed hydrophobic DESs. Moreover, it is of importance to measure the volatility of the DES ratio that will be used.

After the development of solid fundamental knowledge of DESs the future of these liquids will be determined by their efficiency in future applications. More research has to be dedicated to find out whether these DESs perform better than ILs and conventional solvents. On a lab scale it is already clear that many examples will follow and their is a bright future for the field of hydrophobic DES.

Chapter 8

Samenvatting en Suggesties voor Verder Onderzoek

8.1 Samenvatting

Bij veel chemische reacties, het toepassen van scheidingstechnologie (zoals voor extracties en membraanscheidingen), en bijvoorbeeld de productie van emulsies spelen oplosmiddelen nog steeds een essentiële rol. Een nadeel van veel van de huidige oplosmiddelen is de belasting van het milieu en de volksgezondheid. Idealiter worden deze milieubelastende oplosmiddelen vervangen door duurzamere (en innovatievere) oplosmiddelen. Een groep van oplosmiddelen die onderzocht zijn om conventionele oplosmiddelen te vervangen zijn ionische vloeistoffen (ILs), deze zijn bereid door middel van een chemische synthese en moeten dus worden opgezuiverd om bijproducten en startproducten te verwijderen. Dit maakt ze duur en dus minder geschikte vervangers voor conventionele oplosmiddelen die op grote schaal in de chemische industrie worden gebruikt.

In 2003 verschenen de eerste artikels over een nieuwe klasse van innovatieve oplosmiddelen, diep eutectische oplosmiddelen (DESs). Deze DESs hebben vergelijkbare fysisch-chemische eigenschappen als ILs, maar ze hoeven niet opgezuiverd te worden doordat ze eenvoudig gemaakt kunnen worden door de vaste componenten van de DES te mengen. Het voornaamste voordeel is dat ze goedkoop zijn.

Het DES onderzoek in de literatuur concentreerde zich voornamelijk op hydrofiele DESs. Hydrofiele DESs zijn niet of nauwelijks mengbaar met water. Hydrofobe DESs zijn pas in de literatuur geïntroduceerd in 2015; werk dat wordt beschreven in hoofdstuk 2 van dit proefschrift. Het centrale thema van dit proefschrift is de ontdekking, het ontwerp en het toepassen van hydrofobe

DESs, een nieuwe klasse van duurzame en innovatieve niet-water oplosbare oplosmiddelen. Een hydrofobe DES bestaat uit twee niet-water oplosbare vaste stoffen die waarschijnlijk een vloeistof vormen door waterstofbruggen, mengentropie en/of Van der Waals interacties tussen de twee componenten. Hierdoor wordt de smelttemperatuur verlaagt ten opzichte van de smelttemperatuur van de individuele stoffen. Hoofdstuk 1 geeft een eerste inleiding in het veld van DESs, terwijl hoofdstuk 2 is gebaseerd op de eerste publicatie in de literatuur over hydrofobe DESs. Deze DESs bestaan uit decaanzuur en een quaternair ammonium zout. Als anionen van deze zouten zijn zowel bromide als chloride gebruikt. De fysisch-chemische eigenschappen zijn bepaald na bereiding en vergeleken met hydrofiele DESs. De verdeling van de componenten over de DES en waterfase is onderzocht om meer informatie te vinden over de hoeveelheid water die de DES opneemt en de hoeveelheid van de DES componenten die naar de waterfase gaat. Als mogelijke toepassing is onderzocht of deze hydrofobe DESs gebruikt kunnen worden voor het verwijderen van vetzuren uit water.

In hoofdstuk 3 zijn 507 combinaties van vaste stoffen getest die bestaan uit terpenen. Hieruit zijn 17 hydrofobe DESs geproduceerd. Van deze 17 hydrofobe DESs zijn de hoeveelheid water, dichtheid en viscositeit bepaald. Met behulp van nucleaire magnetische resonantie is onderzocht of de twee componenten met elkaar reageren. Thermo-gravimetrische analyse is gebruikt om de ontledingstemperatuur van de DESs te onderzoeken. De duurzaamheid en het toekomstige gebruik werd gekwalificeerd op basis van vier criteria. Deze criteria zijn een dichtheidsverschil met water $\geq 50\,\mathrm{kg\,m^{-3}}$, een viscositeit lager dan $100\ \mathrm{mPa\cdot s}$, overdracht van DES naar de waterfase die zo laag mogelijk is en een verwaarloosbare verandering van de pH van de waterfase tussen de 6 en 8. De resultaten leiden ertoe dat vijf hydrofobe DESs voldoen aan deze voorwaarden. Als laatste is een selectie van deze ontwikkelde hydrofobe DESs gebruikt voor het verwijderen van riboflavine (vitamine B2) uit water. De DESs die in hoofdstuk 2 en 3 zijn ontwikkeld, zijn in de komende hoofdstukken gebruikt voor toepassingen.

Hoofdstuk 4 laat zien dat DESs gemaakt door middel van decaanzuur met een combinatie van quaternaire ammoniumzouten kunnen worden gebruikt voor het afvangen van CO_2. De resultaten laten zien dat de oplosbaarheden van CO_2 afhankelijk zijn van het molair volume van de hydrofobe DESs. Hoe hoger het molaire volume, hoe hoger de oplosbaarheid. Verschillende cycli van absorptie en regeneratie zijn getest waarbij geen verlies van massa van de DES werd waargenomen. De Henry constante werd bepaald om de oplosbaarheden van CO_2 in verschillende oplosmiddelen te bepalen. De resultaten laten zien dat DESs bestaande uit decaanzuur en de ammoniumzouten tetraoctylammonium bromide en tetraoctylammonium chloride een vergelijkbare CO_2 oplosbaarheid hebben als de één na beste ionische vloeistof. Deze oplosbaarheden konden worden voorspeld door een model waarin de onbekende parameters zijn bepaald op basis van dichtheden van de DES. De resultaten laten zien dat het model de oplosbaarheid van CO_2 redelijkerwijs voorspellen.

Hoofdstuk 5 laat het gebruik zien van hydrofobe DESs geproduceerd van decaanzuur en lidocaine voor het verwijderen van metaal ionen uit water. De resultaten laten zien dat transitie metaal ionen efficiënt kunnen worden verwijderd met behulp van deze DES, terwijl het verwijderen van alkali metaal ionen minder makkelijk is. Een experiment waarin een combinatie van transitie en alkali metaal ionen werd onderzocht, laat zien dat de verwijdering van de transitie metaal ionen nog steeds efficiënt is, maar de verwijdering van alkali metaal ionen nog steeds moeizaam is. Maximale verwijdering gebeurt al binnen 5 seconden en er is aangetoond dat regeneratie mogelijk is. Het extractie mechanisme is gebaseerd op ionenwisseling.

Hoofdstuk 6 gaat over het bereiden van olie-in-water emulsies met hydrofobe DES als oliefase. Een emulsie is een verdeling van kleine oliedruppels in water. In dit geval is een zeep gebruikt die met één kant van zijn molecuul graag in de waterfase zit en met de andere kant van het molecuul in de oliefase om de emulsie te stabiliseren. Een bekend voorbeeld van een emulsie is mayonaise. De oliefase van de emulsie is de hydrofobe DES bestaande uit een binair mengsel van 1-tetradecanol en menthol, terwijl natriumdodecylsulfaat is gebruikt als surfactant om de emulsie te stabiliseren. De fysisch-chemische eigenschappen dichtheid, viscositeit en oppervlaktespanning zijn bepaald om deze DES te karakteriseren. Met behulp van microscopie is allereerst geïllustreerd dat er zich DES druppels bevinden in de olie-in-water emulsie. De grootte van de druppels is bepaald met behulp van dynamische lichtverstrooiing. De druppelgrootte neemt toe ten tevolge van Ostwaldrijping. Om inzicht te krijgen in de factoren die Ostwaldrijping beïnvloeden is de concentratie van de natriumdodecylsulfaat, de massa fractie van de DES gevarïeerd en is de toevoeging van zout op de groeisnelheid van de druppels getest. Een verhoging van de concentratie van natriumdodecylsulfaat verlaagt de groeisnelheid van de druppels. Massafracties tot 1.5×10^{-3} laten vergelijkbare groeisnelheden zien doordat er in dit regime sprake is van een verdunde oplossing. Verder laten de resultaten zien dat het toevoegen van zout geen effect heeft op de groeisnelheid van de druppels. Berekeningen van de groeisnelheid van de olie-in-water druppels laten zien dat er vergelijkbare groeisnelheden worden gevonden als in de literatuur.

Door het ontdekken van hydrofobe DESs in 2015 is een nieuw onderzoekgebied gestart op het gebied van niet met water mengbare oplosmiddelen. In dit proefschrift zijn nieuwe hydrofobe DESs ontwikkeld, die als duurzaam kunnen worden beschouwd door hun lage viscositeit, de makkelijke scheiding tussen de DES en water fase, de beperkte uitwisseling van DES en water en het gebruik van natuurlijke componenten. De toekomst zal moeten tonen of ze potentie hebben voor verder gebruik in wetenschappelijk onderzoek en/of ze gebruikt zullen worden door de chemische industrie.

8.2 Suggesties voor verder onderzoek

In dit proefschrift zijn nieuwe, hydrofobe eutectische vloeistoffen en hun eigenschappen beschreven. Tevens zijn er stappen gezet richting het toepassen van deze duurzamere, hydrofobe vloeistoffen. Hieronder worden enkele suggesties gedaan voor vervolgonderzoek dat kan helpen om verdere technologische doorbraken te realiseren. Een belangrijke volgende stap om inzicht te krijgen in de werking van hydrofobe DESs is het doen van fundamenteel onderzoek om beter begrip te creëren omtrent de invloed van intermoleculaire interacties op de vorming van deze DESs. Theoretisch inzicht kan worden verkregen door bijvoorbeeld dichtheidsfunctionaaltheorie berekeningen en moleculaire dynamica simulaties. Daarnaast is systematisch experimenteel werk zoals het construeren van fase diagrammen van zowel het vast-vloeistof evenwicht en het vloeistof-gas evenwicht essentieel om fundamentele kennis van de thermodynamica van DESs te verkrijgen.

Begrip over de vorming van een DES uit twee vaste stoffen en de bijbehorende toepassing zal toekomstig experimenteel onderzoek versnellen. Het is nuttig om modellen te ontwikkelen die met zo weinig mogelijk informatie het fasegedrag van een DES kunnen voorspellen zodat op voorhand kan worden aangegeven welke twee componenten een DES vormen en welke niet. Daarnaast is het nuttig om modellen te ontwikkelen die het gedrag van een DES in toepassingen kunnen voorspellen. In dit proefschrift wordt dit geïllustreerd op basis van een model voor de oplosbaarheid van CO_2 in de hydrofobe DESs. Een model dat kan voorspellen of een DES wordt gevormd in combinatie met een model dat gedrag van DESs in een toepassing, zoals extractie, kan voorspellen zal onderzoekers veel informatie verschaffen en veel tijd besparen.

In dit proefschrift zijn reeds fysisch-chemische eigenschappen en toepassingen van DESs gerapporteerd, maar er is ook kennis over de vorming van DESs gegenereerd. Naast de reeds gemelde modellen zal het echter van belang blijven om systematisch parameters van nieuw ontwikkelde hydrofobe DESs te bepalen, zowel voor als na menging met water. Parameters die van belang zijn:

- De hoeveelheid water in de hydrofobe DESs voor en na mixen met water.
- De dichtheid en viscositeit van de hydrofobe DES voor en na mengen met water.
- Chemische analyse van de DES fase om te onderzoeken of de twee componenten niet met elkaar gereageerd hebben.
- Overdacht van de DES fase naar de water fase via analytische technieken die meer informatie geven over:
    (i) De pH van de water fase, en
    (ii) De hoeveelheid van de DES componenten die naar de waterfase zijn overgedragen (totale organische koolstof, ion chromatografie, nucleaire magnetische resonantie).

Indien emulsies worden gemaakt, moeten de volgende parameters ook worden bepaald:

- Oppervlaktespanning van de DES.
- Grensvlakspanning tussen de DES en de water fase.
- Grensvlakspanning tussen de DES fase en de water fase in aanwezigheid van surfactant.

Ondanks dat het niet onderzocht is in dit proefschrift zou een studie naar de biologische afbreekbaarheid en de toxiciteit van DESs ’standaard’ moeten worden. Daarnaast zou ook de vluchtigheid moeten worden onderzocht van de DES ratio die wordt gebruikt voor toepassingen.

Na de ontwikkeling van solide fundamentele kennis van DESs zal de toekomst van deze vloeistoffen worden bepaald door de efficiëntie van deze vloeistoffen in toepassingen. Meer onderzoek is noodzakelijk om erachter te komen of de DESs beter presteren dan ionische vloeistoffen en conventionele oplosmiddelen. Op labschaal is het reeds duidelijk dat vele voorbeelden nog zullen volgen en dat het hydrofobe DES veld een mooie toekomst tegemoet gaat.

Bibliography

[1] T. Welton, "Solvents and sustainable chemistry," *Proc. R. Soc. A*, vol. 471, p. 20150502, 2015. 2

[2] E. U. climate and energy package. 2

[3] E. U. low carbon economy. 2

[4] P. T. Anastas and J. C. Warner, *Green chemistry: theory and practice*. Oxford university press, 1998. 2, 4, 44

[5] P. Wasserscheid and T. Welton, *Ionic liquids in synthesis*, vol. 1. Weinheim: Wiley Online Library, 2008. 4, 9, 44

[6] H. Olivier-Bourbigou, L. Magna, and D. Morvan, "Ionic liquids and catalysis: Recent progress from knowledge to applications," *Applied Catalysis A: General*, vol. 373, pp. 1–56, 2010. 4

[7] D. R. MacFarlane, N. Tachikawa, M. Forsyth, J. M. Pringle, P. C. Howlett, G. D. Elliott, J. H. Davis, M. Watanabe, P. Simon, and C. A. Angell, "Energy applications of ionic liquids," *Energy & Environmental Science*, vol. 7, pp. 232–250, 2014. 4

[8] M. A. P. Martins, C. P. Frizzo, A. Z. Tier, D. N. Moreira, N. Zanatta, and H. G. Bonacorso, "Ionic liquids in heterocyclic synthesis," *Chemical Reviews*, vol. 114, pp. 2015–2050, 2014. 4

[9] J. P. Hallett and T. Welton, "Room-temperature ionic liquids: solvents for synthesis and catalysis. 2," *Chemical reviews*, vol. 111, pp. 3508–3576, 2011. 4

[10] D. Parmentier, S. J. Metz, and M. C. Kroon, "Tetraalkylammonium oleate and linoleate based ionic liquids: promising extractants for metal salts," *Green Chemistry*, vol. 15, pp. 205–209, 2013. 4, 16, 67, 119, 124

[11] B. Kirchner, "Topics in current chemistry," *Ionic Liquids, Springer-Verlag, New york*, 2009. 4

[12] N. V. Plechkova and K. R. Seddon, "Applications of ionic liquids in the chemical industry," *Chemical Society Reviews*, vol. 37, pp. 123–150, 2008. 4

[13] T. L. Greaves and C. J. Drummond, "Protic ionic liquids: properties and applications," *Chemical reviews*, vol. 108, pp. 206–237, 2008. 4, 5, 6

[14] B. Clare, A. Sirwardana, and D. R. MacFarlane, "Synthesis, purification and characterization of ionic liquids," in *Ionic Liquids*, pp. 1–40, Springer, 2010. 4

[15] M. Pucheault and M. Vaultier, "Task specific ionic liquids and task specific onium salts," in *Ionic Liquids*, pp. 83–126, Springer, 2010. 4

[16] B. Smit, J. A. Reimer, C. M. Oldenburg, and I. C. Bourg, *Introduction to Carbon Capture and Sequestration*. World Scientific, 2014. 6, 16, 82

[17] M. Francisco, A. van den Bruinhorst, and M. C. Kroon, "New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing," *Green Chemistry*, vol. 14, pp. 2153–2157, 2012. 6, 10, 12

[18] D. V. Wagle, H. Zhao, and G. A. Baker, "Deep eutectic solvents: Sustainable media for nanoscale and functional materials," *Accounts of chemical research*, vol. 47, pp. 2299–2308, 2014. 6

[19] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, and Y. H. Choi, "Natural deep eutectic solvents as new potential media for green technology," *Analytica chimica acta*, pp. 61–68, 2013. 7, 10

[20] C. Florindo, F. S. Oliveira, L. P. N. Rebelo, A. M. Fernandes, and I. M. Marrucho, "Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids," *ACS Sustainable Chemistry & Engineering*, vol. 2, pp. 2416–2425, 2014. 7, 9, 10, 44

[21] M. C. Gutierrez, M. L. Ferrer, C. R. Mateo, and F. del Monte, "Freeze-drying of aqueous solutions of deep eutectic solvents: a suitable approach to deep eutectic suspensions of self-assembled structures," *Langmuir*, vol. 25, pp. 5509–5515, 2009. 7, 9

[22] P. M. Dean, J. M. Pringle, and D. R. MacFarlane, "Structural analysis of low melting organic salts: perspectives on ionic liquids," *Physical Chemistry Chemical Physics*, vol. 12, pp. 9144–9153, 2010. 9

[23] D. Rooney, J. Jacquemin, and R. Gardas, "Thermophysical properties of ionic liquids," in *Ionic Liquids*, pp. 185–212, Springer, 2010. 9, 25

[24] C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki, and J. F. Brennecke, "Thermophysical properties of imidazolium-based ionic liquids," *Journal of Chemical & Engineering Data*, vol. 49, pp. 954–964, 2004. 9

[25] H. F. Almeida, H. Passos, J. A. Lopes-da Silva, A. M. Fernandes, M. G. Freire, and J. A. P. Coutinho, "Thermophysical properties of five acetate-based ionic liquids," *Journal of Chemical & Engineering Data*, vol. 57, pp. 3005–3013, 2012. 9

[26] K. N. Marsh, J. A. Boxall, and R. Lichtenthaler, "Room temperature ionic liquids and their mixtures — a review," *Fluid Phase Equilibria*, vol. 219, pp. 93–98, 2004. 9

[27] A. Goodwin, K. N. Marsh, and W. Wakeham, *Measurement of the thermodynamic properties of single phases*. Elsevier, 2003. 9

[28] M. Tariq, J. Esperancca, M. Soromenho, L. Rebelo, and J. C. Lopes, "Shifts in the temperature of maximum density (TMD) of ionic liquid aqueous solutions," *Physical Chemistry Chemical Physics*, vol. 15, pp. 10960–10970, 2013. 9

[29] M. Kanakubo and K. R. Harris, "Density of 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) amide and 1-hexyl-3-methylimidazolium bis (trifluoromethanesulfonyl) amide over an extended pressure range up to 250 MPa," *Journal of Chemical & Engineering Data*, vol. 60, pp. 1408–1418, 2015. 9

[30] X. Wang, Y. Chi, and T. Mu, "A review on the transport properties of ionic liquids," *Journal of Molecular Liquids*, vol. 193, pp. 262–266, 2014. 9

[31] Q. Zhang, K. D. O. Vigier, S. Royer, and F. Jérôme, "Deep eutectic solvents: syntheses, properties and applications," *Chemical Society Reviews*, vol. 41, pp. 7108–7146, 2012. 9, 10, 12, 16

[32] L. F. Zubeir, M. H. Lacroix, and M. C. Kroon, "Low transition temperature mixtures as innovative and sustainable CO_2 capture solvents," *The Journal of Physical Chemistry B*, vol. 118, pp. 14429–14441, 2014. 9, 10, 82, 85, 86, 88, 91

[33] A. P. Abbott, G. Capper, and S. Gray, "Design of improved deep eutectic solvents using hole theory," *Chemphyschem*, vol. 7, pp. 803–806, 2006. 9

[34] A. Hayyan, F. S. Mjalli, I. M. AlNashef, Y. M. Al-Wahaibi, T. Al-Wahaibi, and M. A. Hashim, "Glucose-based deep eutectic solvents: Physical properties," *Journal of Molecular Liquids*, vol. 178, pp. 137–141, 2013. 9

[35] K. Shahbaz, S. Baroutian, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Densities of ammonium and phosphonium based deep eutectic solvents: Prediction using artificial intelligence and group contribution techniques," *Thermochimica Acta*, vol. 527, pp. 59–66, 2012. 9

[36] L. Bahadori, M. H. Chakrabarti, F. S. Mjalli, I. M. AlNashef, N. S. A. Manan, and M. A. Hashim, "Physicochemical properties of ammonium-based deep eutectic solvents and their electrochemical evaluation using organometallic reference redox systems," *Electrochimica Acta*, vol. 113, pp. 205–211, 2013. 9

[37] A. P. Abbott, R. C. Harris, K. S. Ryder, C. D'Agostino, L. F. Gladden, and M. D. Mantle, "Glycerol eutectics as sustainable solvent systems," *Green Chemistry*, vol. 13, pp. 82–90, 2011. 9

[38] K. Shahbaz, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Prediction of deep eutectic solvents densities at different temperatures," *Thermochimica Acta*, vol. 515, pp. 67–72, 2011. 9

[39] D. R. Lide, *CRC handbook of chemistry and physics*. London: CRC press, 2004. 9

[40] S. Aparicio, M. Atilhan, and F. Karadas, "Thermophysical properties of pure ionic liquids: review of present situation," *Industrial & Engineering Chemistry Research*, vol. 49, pp. 9580–9595, 2010. 9

[41] A. Bhattacharjee, P. J. Carvalho, and J. A. P. Coutinho, "The effect of the cation aromaticity upon the thermophysical properties of piperidinium-and pyridinium-based ionic liquids," *Fluid Phase Equilibria*, vol. 375, pp. 80–88, 2014. 9

[42] A. Bhattacharjee, J. A. Lopes-da Silva, M. G. Freire, J. A. P. Coutinho, and P. J. Carvalho, "Thermophysical properties of phosphonium-based ionic liquids," *Fluid Phase Equilibria*, vol. 400, pp. 103–113, 2015. 9

[43] M. A. R. Martins, C. M. S. S. Neves, K. A. Kurnia, A. Luís, L. M. N. B. F. Santos, M. G. Freire, S. P. Pinho, and J. A. P. Coutinho, "Impact of the cation symmetry on the mutual solubilities between water and imidazolium-based ionic liquids," *Fluid Phase Equilibria*, vol. 375, pp. 161–167, 2014. 9

[44] M. A. R. Martins, C. M. S. S. Neves, K. A. Kurnia, P. J. Carvalho, M. A. A. Rocha, L. M. N. B. F. Santos, S. P. Pinho, and M. G. Freire, "Densities, viscosities and derived thermophysical properties of water-saturated imidazolium-based ionic liquids," *Fluid Phase Equilibria*, vol. 407, pp. 188–196, 2016. 9

[45] J. Jacquemin, P. Husson, A. A. H. Padua, and V. Majer, "Density and viscosity of several pure and water-saturated ionic liquids," *Green Chemistry*, vol. 8, pp. 172–180, 2006. 9

[46] S. N. Baker, G. A. Baker, and F. V. Bright, "Temperature-dependent microscopic solvent properties of 'dry'and 'wet' 1-butyl-3-methylimidazolium hexafluorophosphate: correlation with ET (30) and Kamlet–Taft polarity scales," *Green Chemistry*, vol. 4, pp. 165–169, 2002. 9

[47] J. A. Widegren, A. Laesecke, and J. W. Magee, "The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids," *Chemical communications*, pp. 1610–1612, 2005. 9

[48] S. Saha and H. Hamaguchi, “Effect of water on the molecular structure and arrangement of nitrile-functionalized ionic liquids,” *The Journal of Physical Chemistry B*, vol. 110, pp. 2777–2781, 2006. 9

[49] A. P. Abbott, R. C. Harris, and K. S. Ryder, “Application of hole theory to define ionic liquids by their transport properties,” *The Journal of Physical Chemistry B*, vol. 111, pp. 4910–4913, 2007. 9

[50] Y. Dai, G.-J. Witkamp, R. Verpoorte, and Y. H. Choi, “Tailoring properties of natural deep eutectic solvents with water to facilitate their applications,” *Food chemistry*, vol. 187, pp. 14–19, 2015. 9

[51] D. Shah and F. S. Mjalli, “Effect of water on the thermo-physical properties of reline: An experimental and molecular simulation based approach,” *Physical Chemistry Chemical Physics*, vol. 16, pp. 23900–23907, 2014. 9

[52] S. Matsuo and T. Makita, “Viscosities of six 1-alkanols at temperatures in the range 298–348 k and pressures up to 200 MPa,” *International journal of thermophysics*, vol. 10, pp. 833–843, 1989. 9

[53] M. Tariq, P. J. Carvalho, J. A. P. Coutinho, I. M. Marrucho, J. N. C. Lopes, and L. P. Rebelo, “Viscosity of (C2–C14) 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) amide ionic liquids in an extended temperature range,” *Fluid Phase Equilibria*, vol. 301, pp. 22–32, 2011. 9

[54] J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, S. Johnson, K. R. Seddon, and R. D. Rogers, “Crystal polymorphism in 1-butyl-3-methylimidazolium halides: supporting ionic liquid formation by inhibition of crystallization,” *Chemical Communications*, pp. 1636–1637, 2003. 10

[55] C. Hardacre, J. D. Holbrey, P. B. McCormac, S. E. J. McMath, M. Nieuwenhuyzen, and K. R. Seddon, “Crystal and liquid crystalline polymorphism in 1-alkyl-3-methylimidazolium tetrachloropalladate (ii) salts,” *Journal of Materials Chemistry*, vol. 11, pp. 346–350, 2001. 10

[56] W. A. Henderson, P. Fylstra, C. Hugh, P. C. Trulove, and S. Parsons, “Crystal structure of the ionic liquid EtNH3NO3—insights into the thermal phase

behavior of protic ionic liquids," *Physical Chemistry Chemical Physics*, vol. 14, pp. 16041–16046, 2012. 10

[57] E. L. Smith, A. P. Abbott, and K. S. Ryder, "Deep eutectic solvents (DESs) and their applications," *Chemical reviews*, vol. 114, pp. 11060–11082, 2014. 10, 12, 44

[58] M. Francisco, A. van den Bruinhorst, and M. C. Kroon, "Low-transition-temperature mixtures (LTTMs): a new generation of designer solvents," *Angewandte Chemie (International ed. in English)*, vol. 52, pp. 3074–3085, 2013. 10, 11, 12, 16, 24, 44, 56

[59] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R. L. Reis, and A. R. C. Duarte, "Natural deep eutectic solvents – solvents for the 21st century," *ACS Sustainable Chemistry & Engineering*, vol. 2, pp. 1063–1071, 2014. 10, 11

[60] X. Baokou and M. Anouti, "Physical properties of a new deep eutectic solvent based on a sulfonium ionic liquid as a suitable electrolyte for electric double-layer capacitors," *The Journal of Physical Chemistry C*, vol. 119, pp. 970–979, 2014. 10

[61] M. Francisco, A. van den Bruinhorst, L. F. Zubeir, C. J. Peters, and M. C. Kroon, "A new low transition temperature mixture (LTTM) formed by choline chloride + lactic acid: characterization as solvent for CO_2 capture," *Fluid Phase Equilibria*, vol. 340, pp. 77–84, 2013. 10, 82

[62] N. Gathergood, M. T. Garcia, and P. J. Scammells, "Biodegradable ionic liquids: Part i. Concept, preliminary targets and evaluation," *Green Chemistry*, vol. 6, pp. 166–175, 2004. 10

[63] M. T. Garcia, N. Gathergood, and P. J. Scammells, "Biodegradable ionic liquids Part ii. Effect of the anion and toxicology," *Green Chemistry*, vol. 7, pp. 9–14, 2005. 10

[64] N. Gathergood, P. J. Scammells, and M. T. Garcia, "Biodegradable ionic liquids Part iii. The first readily biodegradable ionic liquids," *Green Chemistry*, vol. 8, pp. 156–160, 2006. 10

[65] D. Coleman and N. Gathergood, "Biodegradation studies of ionic liquids," *Chemical Society reviews*, vol. 39, pp. 600–637, 2010. 10

[66] B. Kudłak, K. Owczarek, and J. Namieśnik, "Selected issues related to the toxicity of ionic liquids and deep eutectic solvents – a review," *Environmental Science and Pollution Research*, vol. 22, pp. 11975–11992, 2015. 10, 11

[67] Y. H. Choi, J. van Spronsen, Y. Dai, M. Verberne, F. Hollmann, I. W. C. E. Arends, G.-J. Witkamp, and R. Verpoorte, "Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology?," *Plant physiology*, vol. 156, pp. 1701–1705, 2011. 11

[68] S. P. M. Ventura, R. L. F. de Barros, T. Sintra, C. M. Soares, A. S. Lima, and J. A. Coutinho, "Simple screening method to identify toxic/non-toxic ionic liquids: Agar diffusion test adaptation," *Ecotoxicology and environmental safety*, vol. 83, pp. 55–62, 2012. 11

[69] M. Hayyan, M. A. Hashim, M. A. Al-Saadi, A. Hayyan, I. M. AlNashef, and M. E. S. Mirghani, "Assessment of cytotoxicity and toxicity for phosphonium-based deep eutectic solvents," *Chemosphere*, vol. 93, pp. 455–9, 2013. 11, 46

[70] K. Radošević, M. C. Bubalo, V. G. Srček, D. Grgas, T. L. Dragičević, and I. R. Redovniković, "Evaluation of toxicity and biodegradability of choline chloride based deep eutectic solvents," *Ecotoxicology and environmental safety*, vol. 112, pp. 46–53, 2015. 11, 46

[71] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, and Y. H. Choi, "Natural deep eutectic solvents as new potential media for green technology," *Analytica chimica acta*, vol. 766, pp. 61–68, 2013. 11

[72] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R. L. Reis, and A. R. C. Duarte, "Natural deep eutectic solvents – solvents for the 21st century," *ACS Sustainable Chemistry & Engineering*, vol. 2, pp. 1063–1071, 2014. 11, 45, 46

[73] D. J. G. P. van Osch, L. J. B. M. Kollau, A. van den Bruinhorst, S. Asikainen, M. A. A. Rocha, and M. C. Kroon, "Ionic liquids and deep eutectic solvents

for lignocellulosic biomass fractionation," *Physical Chemistry Chemical Physics*, vol. 19, pp. 2636–2665, 2017. 12

[74] G. Tian, "Application of ionic liquids in extraction and separation of metals," in *Green Solvents II*, pp. 119–153, Springer, 2012. 16

[75] N. R. Rodriguez, B. S. Molina, and M. C. Kroon, "Aliphatic + ethanol separation via liquid–liquid extraction using low transition temperature mixtures as extracting agents," *Fluid Phase Equilibria*, vol. 394, pp. 71–82, 2015. 16

[76] C. Li, D. Li, S. Zou, Z. Li, J. Yin, A. Wang, Y. Cui, Z. Yao, and Q. Zhao, "Extraction desulfurization process of fuels with ammonium-based deep eutectic solvents," *Green Chemistry*, vol. 15, pp. 2793–2799, 2013. 16

[77] K. Bica, J. Shamshina, W. L. Hough, D. R. MacFarlane, and R. D. Rogers, "Liquid forms of pharmaceutical co-crystals: exploring the boundaries of salt formation," *Chemical Communications*, vol. 47, pp. 2267–2269, 2011. 16, 105

[78] P. J. Griffin, T. Cosby, A. P. Holt, R. S. Benson, and J. R. Sangoro, "Charge transport and structural dynamics in carboxylic-acid-based deep eutectic mixtures," *The Journal of Physical Chemistry B*, vol. 118, pp. 9378–9385, 2014. 16, 24, 105, 113

[79] B. D. Ribeiro, C. Florindo, L. C. Iff, M. A. Z. Coelho, and I. M. Marrucho, "Menthol-based eutectic mixtures: hydrophobic low viscosity solvents," *ACS Sustainable Chemistry & Engineering*, vol. 3, pp. 2469–2477, 2015. 16, 44, 56

[80] E. E. Tereshatov, M. Y. Boltoeva, and C. M. Folden, "First evidence of metal transfer into hydrophobic deep eutectic and low-transition-temperature mixtures: indium extraction from hydrochloric and oxalic acids," *Green Chemistry*, vol. 18, pp. 4616–4622, 2016. 16, 44, 105

[81] C. H. J. T. Dietz, M. C. Kroon, M. Di Stefano, M. van Sint Annaland, and F. Gallucci, "Selective separation of furfural and hydroxymethylfurfural from an aqueous solution using a supported hydrophobic deep eutectic

solvent liquid membrane," *Faraday discussions*, vol. 206, pp. 77–92, 2017. 16, 44, 50, 136

[82] M. B. Arain, E. Yilmaz, and M. Soylak, "Deep eutectic solvent based ultrasonic assisted liquid phase microextraction for the faas determination of cobalt," *Journal of Molecular Liquids*, vol. 224, pp. 538–543, 2016. 16, 44

[83] S. Zhu, J. Zhou, H. Jia, and H. Zhang, "Liquid–liquid microextraction of synthetic pigments in beverages using a hydrophobic deep eutectic solvent," *Food chemistry*, vol. 243, pp. 351–356, 2018. 16, 44, 136

[84] J. Cao, M. Yang, F. Cao, J. Wang, and E. Su, "Well-designed hydrophobic deep eutectic solvents as green and efficient media for the extraction of artemisinin from artemisia annua leaves," *ACS Sustainable Chemistry & Engineering*, vol. 5, pp. 3270–3278, 2017. 16, 44, 136

[85] E. L. P. de Faria, R. S. do Carmo, A. F. M. Cláudio, C. S. R. Freire, M. G. Freire, and A. J. D. Silvestre, "Deep eutectic solvents as efficient media for the extraction and recovery of cynaropicrin from cynara cardunculus l. leaves," *International journal of molecular sciences*, vol. 18, p. 2276, 2017. 16, 44, 136

[86] A. W. Ralston and C. W. Hoerr, "The solubilities of the normal saturated fatty acids," *The Journal of Organic Chemistry*, vol. 7, pp. 546–555, 1942. 17

[87] M. A. A. Rocha, C. M. S. S. Neves, M. G. Freire, O. Russina, A. Triolo, J. A. Coutinho, and L. M. N. B. F. Santos, "Alkylimidazolium based ionic liquids: impact of cation symmetry on their nanoscale structural organization," *The Journal of Physical Chemistry B*, vol. 117, pp. 10889–10897, 2013. 25

[88] M. A. A. Rocha, F. M. S. Ribeiro, A. I. M. C. L. Ferreira, J. A. Coutinho, and L. M. N. B. F. Santos, "Thermophysical properties of [CN-1C1im][PF6] ionic liquids," *Journal of Molecular Liquids*, vol. 188, pp. 196–202, 2013. 25, 26, 113, 115

[89] L. F. Zubeir, M. A. A. Rocha, N. Vergadou, W. M. Weggemans, L. D. Peristeras, P. S. Schulz, I. G. Economou, and M. C. Kroon, "Thermophysical properties of imidazolium tricyanomethanide ionic liquids: experiments

and molecular simulation," *Physical Chemistry Chemical Physics*, vol. 18, pp. 23121–23138, 2016. 25, 26, 113, 115

[90] V. S. Kislik, *Solvent extraction: classical and novel approaches*. Elsevier, 2012. 30

[91] S. T. Yang, S. A. White, and S. T. Hsu, "Extraction of carboxylic acids with tertiary and quaternary amines: effect of pH," *Industrial & Engineering Chemistry Research*, vol. 30, pp. 1335–1342, 1991. 31

[92] T. P. T. Pham, C.-W. Cho, and Y.-S. Yun, "Environmental fate and toxicity of ionic liquids: a review," *Water research*, vol. 44, pp. 352–372, 2010. 44

[93] D. Zhao, Y. Liao, and Z. Zhang, "Toxicity of ionic liquids," *Clean-soil, air, water*, vol. 35, pp. 42–48, 2007. 44

[94] A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, and V. Tambyrajah, "Novel solvent properties of choline chloride/urea mixtures," *Chemical Communications*, pp. 70–71, 2003. 44

[95] D. J. G. P. van Osch, L. F. Zubeir, A. van den Bruinhorst, M. A. A. Rocha, and M. C. Kroon, "Hydrophobic deep eutectic solvents as water-immiscible extractants," *Green Chemistry*, vol. 17, pp. 4518–4521, 2015. 44, 56, 59, 86, 93, 136

[96] D. J. G. P. van Osch, D. Parmentier, C. H. J. T. Dietz, A. van den Bruinhorst, R. Tuinier, and M. C. Kroon, "Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents," *Chemical Communications*, vol. 52, pp. 11987–11990, 2016. 44, 136

[97] C. H. J. T. Dietz, D. J. G. P. van Osch, M. C. Kroon, G. Sadowski, M. van Sint Annaland, F. Gallucci, L. F. Zubeir, and C. Held, "PC-SAFT modeling of CO_2 solubilities in hydrophobic deep eutectic solvents," *Fluid Phase Equilibria*, vol. 448, pp. 94–98, 2017. 44, 136

[98] L. F. Zubeir, D. J. G. P. Van Osch, M. A. A. Rocha, F. Banat, and M. C. Kroon, "Carbon dioxide solubilities in decanoic acid-based hydrophobic deep eutectic solvents," *Journal of Chemical & Engineering Data*, vol. 63, pp. 913–919, 2018. 44, 96, 136

[99] Y. Liu, J. B. Friesen, J. B. McAlpine, D. C. Lankin, S.-N. Chen, and G. F. Pauli, "Natural deep eutectic solvents: Properties, applications, and perspectives," *Journal of natural products*, vol. 81, pp. 679–690, 2018. 45, 46

[100] Y. Corvis, P. Négrier, M. Lazerges, S. Massip, J.-M. Léger, and P. Espeau, "Lidocaine/l-menthol binary system: cocrystallization versus solid-state immiscibility," *The Journal of Physical Chemistry B*, vol. 114, pp. 5420–5426, 2010. 45

[101] L. Kang, H. W. Jun, and J. W. McCall, "Physicochemical studies of lidocaine–menthol binary systems for enhanced membrane transport," *International journal of pharmaceutics*, vol. 206, pp. 35–42, 2000. 45

[102] L. Kang, H. W. Jun, and N. Mani, "Preparation and characterization of two-phase melt systems of lidocaine," *International journal of pharmaceutics*, vol. 222, pp. 35–44, 2001. 45

[103] Q. Wen, J.-X. Chen, Y.-L. Tang, J. Wang, and Z. Yang, "Assessing the toxicity and biodegradability of deep eutectic solvents," *Chemosphere*, vol. 132, pp. 63–69, 2015. 46

[104] C. Maton, N. De Vos, and C. V. Stevens, "Ionic liquid thermal stabilities: decomposition mechanisms and analysis tools," *Chemical Society Reviews*, vol. 42, pp. 5963–5977, 2013. 59

[105] T. J. Wooster, K. M. Johanson, K. J. Fraser, D. R. MacFarlane, and J. L. Scott, "Thermal degradation of cyano containing ionic liquids," *Green Chemistry*, vol. 8, pp. 691–696, 2006. 59

[106] D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans, and M. C. Kroon, "Selective extraction of metals from chloride solutions with the tetraoctylphosphonium oleate ionic liquid," *Industrial & Engineering Chemistry Research*, vol. 54, pp. 5149–5158, 2015. 67, 105, 117, 118, 119, 124

[107] M. G. Freire, C. M. S. S. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I. M. Marrucho, L. M. Santos, and J. A. P. Coutinho, "Mutual solubilities of water and hydrophobic ionic liquids," *The Journal of Physical Chemistry B*, vol. 111, pp. 13082–13089, 2007. 67

[108] J. Albo, P. Luis, and A. Irabien, "Carbon dioxide capture from flue gases using a cross-flow membrane contactor and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate," *Industrial & Engineering Chemistry Research*, vol. 49, pp. 11045–11051, 2010. 82

[109] C.-H. Yu, C.-H. Huang, and C.-S. Tan, "A review of CO_2 capture by absorption and adsorption," *Aerosol Air Qual. Res*, vol. 12, pp. 745–769, 2012. 82

[110] J. L. Anthony, J. L. Anderson, E. J. Maginn, and J. F. Brennecke, "Anion effects on gas solubility in ionic liquids," *The Journal of Physical Chemistry B*, vol. 109, pp. 6366–6374, 2005. 82, 91

[111] X. Li, M. Hou, B. Han, X. Wang, and L. Zou, "Solubility of CO_2 in a choline chloride + urea eutectic mixture," *Journal of Chemical & Engineering Data*, vol. 53, pp. 548–550, 2008. 82, 91

[112] R. B. Leron and M.-H. Li, "Solubility of carbon dioxide in a choline chloride–ethylene glycol based deep eutectic solvent," *Thermochimica acta*, vol. 551, pp. 14–19, 2013. 82

[113] E. Ali, M. K. Hadj-Kali, S. Mulyono, I. Alnashef, A. Fakeeha, F. Mjalli, and A. Hayyan, "Solubility of CO_2 in deep eutectic solvents: experiments and modelling using the Peng–Robinson equation of state," *Chemical Engineering Research and Design*, vol. 92, pp. 1898–1906, 2014. 82

[114] L. F. Zubeir, C. Held, G. Sadowski, and M. C. Kroon, "PC-SAFT modeling of CO_2 solubilities in deep eutectic solvents," *The Journal of Physical Chemistry B*, vol. 120, pp. 2300–2310, 2016. 83, 86, 90, 92, 94, 95

[115] J. Gross and G. Sadowski, "Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules," *Industrial & engineering chemistry research*, vol. 40, pp. 1244–1260, 2001. 86

[116] J. Gross and G. Sadowski, "Application of the perturbed-chain SAFT equation of state to associating systems," *Industrial & engineering chemistry research*, vol. 41, pp. 5510–5515, 2002. 86

[117] J. A. Barker and D. Henderson, "Perturbation theory and equation of state for fluids: The square-well potential," *The Journal of Chemical Physics*, vol. 47, pp. 2856–2861, 1967. 86

[118] J. A. Barker and D. Henderson, "Perturbation theory and equation of state for fluids. ii. A successful theory of liquids," *The Journal of chemical physics*, vol. 47, pp. 4714–4721, 1967. 86

[119] X. Ji, C. Held, and G. Sadowski, "Modeling imidazolium-based ionic liquids with ePC-SAFT," *Fluid Phase Equilibria*, vol. 335, pp. 64–73, 2012. 86, 93

[120] A. P. Carneiro, O. Rodríguez, C. Held, G. Sadowski, and E. A. Macedo, "Density of mixtures containing sugars and ionic liquids: experimental data and PC-SAFT modeling," *Journal of Chemical & Engineering Data*, vol. 59, pp. 2942–2954, 2014. 86

[121] V. N. Emel'yanenko, D. H. Zaitsau, E. Shoifet, F. Meurer, S. P. Verevkin, C. Schick, and C. Held, "Benchmark thermochemistry for biologically relevant adenine and cytosine. A combined experimental and theoretical study," *The Journal of Physical Chemistry A*, vol. 119, pp. 9680–9691, 2015. 86

[122] J. Palomar, M. Gonzalez-Miquel, A. Polo, and F. Rodriguez, "Understanding the physical absorption of CO_2 in ionic liquids using the COSMO-RS method," *Industrial & Engineering Chemistry Research*, vol. 50, pp. 3452–3463, 2011. 87

[123] Y. Xu, R. P. Schutte, and L. G. Hepler, "Solubilities of carbon dioxide, hydrogen sulfide and sulfur dioxide in physical solvents," *The Canadian Journal of Chemical Engineering*, vol. 70, pp. 569–573, 1992. 91

[124] E. Wilhelm and R. Battino, "Thermodynamic functions of the solubilities of gases in liquids at 25. deg.," *Chemical Reviews*, vol. 73, pp. 1–9, 1973. 91

[125] M. Kleiner and G. Sadowski, "Modeling of polar systems using PCP-SAFT: An approach to account for induced-association interactions," *The Journal of Physical Chemistry C*, vol. 111, pp. 15544–15553, 2007. 93

[126] T. R. Martin and D. M. Holdich, "The acute lethal toxicity of heavy metals to peracarid crustaceans (with particular reference to fresh-water asellids and gammarids)," *Water Research*, vol. 20, pp. 1137–1147, 1986. 104

[127] P. Madoni and M. G. Romeo, "Acute toxicity of heavy metals towards freshwater ciliated protists," *Environmental Pollution*, vol. 141, pp. 1–7, 2006. 104

[128] J. Rydberg, *Solvent extraction principles and practice, revised and expanded*. CRC Press, 2004. 104

[129] S. Wellens, B. Thijs, and K. Binnemans, "An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids," *Green Chemistry*, vol. 14, pp. 1657–1665, 2012. 104

[130] M. L. Dietz, "Ionic liquids as extraction solvents: Where do we stand?," *Separation Science and Technology*, vol. 41, pp. 2047–2063, 2006. 104

[131] E. Norkus, J. Vaičiūnienė, and T. Vuorinen, "Removal of transition metals from alkaline suspensions of cellulose pulp using cdta as chelating agent," *Carbohydrate polymers*, vol. 66, pp. 316–320, 2006. 104

[132] R. Susilo, R. Chandraghatgi, and P. Englezos, "Partitioning of iron, manganese, copper between fibres and liquor and the role of water chemistry," *PULP & PAPER-CANADA*, vol. 106, pp. 47–50, 2005. 104

[133] J. S. Preston, "Solvent extraction of metals by carboxylic acids," *Hydrometallurgy*, vol. 14, pp. 171–188, 1985. 117, 118

[134] D. Parmentier, S. Paradis, S. J. Metz, S. K. Wiedmer, and M. C. Kroon, "Continuous process for selective metal extraction with an ionic liquid," *Chemical Engineering Research and Design*, vol. 109, pp. 553–560, 2016. 123

[135] D. Parmentier, Y. A. Valia, S. J. Metz, O. S. Burheim, and M. C. Kroon, "Regeneration of the ionic liquid tetraoctylammonium oleate after metal extraction," *Hydrometallurgy*, vol. 158, pp. 56–60, 2015. 123

[136] D. Parmentier, T. Vander Hoogerstraete, D. Banerjee, Y. A. Valia, S. J. Metz, K. Binnemans, and M. C. Kroon, "A mechanism for solvent extraction of first row transition metals from chloride media with the ionic liquid tetraoctylammonium oleate," *Dalton Transactions*, vol. 45, pp. 9661–9668, 2016. 124

[137] J. Lyklema, *Fundamentals of Interface and Colloid Science: Soft Colloids*, vol. 5. Elsevier, 2005. 136, 139

[138] T. F. Tadros, *Emulsion Formation and Stability*. John Wiley & Sons, 2013. 136

[139] B. P. Binks and C. P. Whitby, "Silica particle-stabilized emulsions of silicone oil and water: aspects of emulsification," *Langmuir*, vol. 20, pp. 1130–1137, 2004. 136

[140] L. Prince, *Microemulsions Theory and Practice*. Elsevier, 2012. 136

[141] A. Gupta, H. B. Eral, T. A. Hatton, and P. S. Doyle, "Nanoemulsions: formation, properties and applications," *Soft Matter*, vol. 12, pp. 2826–2841, 2016. 136

[142] B. P. Binks, A. K. F. Dyab, and P. D. Fletcher, "Novel emulsions of ionic liquids stabilised solely by silica nanoparticles," *Chemical Communications*, pp. 2540–2541, 2003. 136

[143] M. Pal, R. Rai, A. Yadav, R. Khanna, G. A. Baker, and S. Pandey, "Self-aggregation of sodium dodecyl sulfate within (choline chloride + urea) deep eutectic solvent," *Langmuir*, vol. 30, pp. 13191–13198, 2014. 136

[144] S. J. Rehfeld, "Adsorption of sodium dodecyl sulfate at various hydrocarbon-water interfaces," *The Journal of Physical Chemistry*, vol. 71, pp. 738–745, 1967. 138

[145] J. Soma and K. D. Papadopoulos, "Ostwald ripening in sodium dodecyl sulfate-stabilized decane-in-water emulsions," *Journal of Colloid and Interface Science*, vol. 181, pp. 225–231, 1996. 138, 150, 153

[146] P. Taylor, "Ostwald ripening in emulsions," *Advances in Colloid and Interface Science*, vol. 75, pp. 107–163, 1998. 139

[147] L. I. Rolo, A. I. Caco, A. J. Queimada, I. M. Marrucho, and J. A. P. Coutinho, "Surface tension of heptane, decane, hexadecane, eicosane, and some of their binary mixtures," *Journal of Chemical & Engineering Data*, vol. 47, pp. 1442–1445, 2002. 145, 146

[148] A. S. Kabalnov, A. V. Pertzov, and E. D. Shchukin, "Ostwald ripening in emulsions: I. Direct observations of ostwald ripening in emulsions," *Journal of Colloid and Interface Science*, vol. 118, pp. 590–597, 1987. 153

[149] J. Weiss, N. Herrmann, and D. J. McClements, "Ostwald ripening of hydrocarbon emulsion droplets in surfactant solutions," *Langmuir*, vol. 15, pp. 6652–6657, 1999. 153, 155

[150] E. Nazarzadeh, T. Anthonypillai, and S. Sajjadi, "On the growth mechanisms of nanoemulsions," *Journal of Colloid and Interface Science*, vol. 397, pp. 154–162, 2013. 154

List of Publications

Publications

11. Dannie J.G.P. van Osch, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, Oil-in-Water Emulsions Prepared with a Hydrophobic Deep Eutectic Solvent, *in preparation*

10. Dannie J.G.P. van Osch[1], Carin H.J.T. Dietz[1], Jaap van Spronsen, Maaike Kroon, Fausto Galucci, Martin van Sint Annaland, Remco Tuinier, A Search for Sustainable Hydrophobic Deep Eutectic Solvents, *submitted to ACS Sustainable Chem. Eng.*

9. Adriaan van den Bruinhorst, Nerea R. Rodriguez, Lawien F. Zubeir, Dannie J.G.P. van Osch, Laura J.B.M. Kollau, Marisa A.A. Rocha, Maaike C. Kroon, A Systematic Evaluation of Deep Eutectic Solvent Formation, Stability, and Physicochemical Properties, *in preparation*

8. Samah E.E. Warrag, Dannie J.G.P. van Osch, Cornelus J. Peters, Maaike C. Kroon, Mercury Capture from Petroleum Using Deep Eutectic Solvents, *Ind. Eng. Chem. Res.*, 2018, **57**, 9222-9230

7. Lawien F. Zubeir[1], Dannie J.G.P. van Osch[1], Adriaan van den Bruinhorst, Marisa A.A. Rocha, Maaike C. Kroon, Carbon Dioxide Solubilities in Decanoic Acid-Based Hydrophobic Deep Eutectic Solvents, *J. Chem. Eng. Data*, 2018, **63**, 913-919

6. Carin H.J.T. Dietz[1], Dannie J.G.P van Osch[1], Maaike C. Kroon, Gabriele Sadowski, Martin van Sint Annaland, Fausto Gallucci, Lawien F. Zubeir, Christoph Held, PC-SAFT modeling of CO_2 solubilities in hydrophobic deep eutectic solvents, *Fluid Phase Equilib.*, 2017, **448**, 94-98

5. Dannie J.G.P. van Osch, Laura J.B.M. Kollau, Adriaan van den Bruinhorst, Marisa A.A. Rocha, Maaike C. Kroon, Lignocellulosic Biomass Fractionation by Means of Novel Solvents: Ionic Liquids vs. Deep Eutectic Solvents, *Phys. Chem. Chem. Phys.*, 2017, **19**, 2636-2665

4. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents, *Chem. Commun.*, 2016, **52**, 11987-11990

3. Dannie J. G. P. van Osch[1], Lawien F. Zubeir[1], Adriaan van den Bruinhorst, Marisa A.A. Rocha, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents as Water-immiscible Extractants, *Green Chem.*, 2015, 17, 4518-4521

2. Natan J.W. Straathof, Dannie J.G.P. van Osch, Arian Schouten, Xiao Wang, Jaap C. Schouten, Volker Hessel, Timothy Noël, Photochemical Metal-Free Perfluoroalkylation of Heteroarenes in Continuous Flow, *J. Flow Chem.*, 2014, **4**, 12-17.

1. Hiroki Kobayashi, Brian Driessen, Dannie J.G.P van Osch, Ali Talla, Shinichi Ookawara, Timothy Noël, Volker Hessel, The impact of Novel Process Windows on the Claisen rearrangement, *Tetrahedron*, 2013, **69**, 2885-2890

[1] combined first authorship

Oral presentations at scientific conferences

20. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Dries Parmentier, Carin H.J.T. Dietz, Marjorie G. du Pree, Nicole M.W. van der Heijden Jaap van Spronsen, Marisa A.A. Rocha, Maaike C. Kroon, Mark Vis, A. Catarina C. Esteves, Martin van Sint Annaland, Fausto Gallucci, Remco Tuinier, Mark Vis, Design and Applications of Hydrophobic Deep Eutectic Solvents, *oral presentation, 27th Conference on Molten Salts and Ionic Liquids, October 7th – October 12th, Centro Cultural de Bélem, Lisbon, Portugal*

19. Dannie J.G.P. van Osch, Lawien F. Zubeir, Dries Parmentier, Adriaan van den Bruinhorst, Carin H.J.T. Dietz, Marisa A.A. Rocha, Marjorie G. du Pree, Nicole M.W. van der Heijden, Mark Vis, A. Catarina C. Esteves, Jaap van Spronsen, Remco Tuinier, Maaike C. Kroon, Design and Applications of Hydrophobic Deep Eutectic Solvents, *oral presentation, International Symposium on Solubility Phenomena (ISSP 2018), July 15th – July 20th, Hôtel Oceania l'Univers, Tours, France*

18. Dannie J.G.P. van Osch, Marjorie G. du Pree, Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, The Discovery of Novel Hydrophobic Deep Eutectic Solvent in Water Emulsions, *flash-oral presentation, International Symposium on Solubility Phenomena (ISSP 2018), July 15th – July 20th, Hôtel Oceania l'Univers, Tours, France*

17. Dannie J.G.P. van Osch, Marjorie G. du Pree Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, A Surfactant Based Deep Eutectic Solvents for the Production of DES in H_2O emulsions, *flash-oral presentation, International Symposium on Solubility Phenomena (ISSP 2018), July 15th – July 20th, Hôtel Oceania l'Univers, Tours, France*

16. Dannie J.G.P. van Osch, Marjorie G. du Pree, Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, The Discovery of Novel Hydrophobic Deep Eutectic Solvent

in Water Emulsions, *oral presentation, 16th Conference of the International Association of Colloid and Interface Scientist (IACIS 2018), May 21st – May 25th, Postillion Convention Centre WTC Rotterdam, Rotterdam, the Netherlands*

15. Dannie J.G.P. van Osch, Marjorie G. du Pree, Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, Surfactant Based Deep Eutectic Solvents for the Formation of Emulsions, *soundbite presentation, 16th Conference of the International Association of Colloid and Interface Scientist (IACIS 2018), May 21st – May 25th, Postillion Convention Centre WTC Rotterdam, Rotterdam, the Netherlands*

14. Dannie J.G.P. van Osch, Lawien F. Zubeir, Dries Parmentier, Adriaan van den Bruinhorst, Carin H.J.T. Dietz, Marisa A.A. Rocha, Nicole M.W. van der Heijden, Mark Vis, A. Catarina C. Esteves, Jaap van Spronsen, Remco Tuinier, Maaike C. Kroon, Design and Applications of Hydrophobic Deep Eutectic Solvents, *pitch, 'Energy - Research Meet' (Strategic Area Energy), January 26th, Eindhoven University of Technology, Eindhoven, The Netherlands*

13. Dannie J.G.P. van Osch, Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, First Proof of Self-Assembly of Block Copolymers in a DES: Hydrophilic vs. Hydrophobic, *oral presentation, 2017 AICHE Annual Meeting, October 29th – November 2nd, Minneapolis Convention Center, Minneapolis, MN, United States of America*

12. Dannie J.G.P. van Osch, Dries Parmentier, Adriaan van den Bruinhorst, Carin H.J.T. Dietz, Remco Tuinier, Maaike C. Kroon, First Principles of Metal Ion Extraction from Non-Buffered Water with Hydrophobic Deep Eutectic Solvents, *oral presentation, 2017 AICHE Annual Meeting, October 29th – November 2nd, Minneapolis Convention Center, Minneapolis, MN, United States of America*

11. Dannie J.G.P. van Osch, Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, The Discovery of Novel Hydrophobic DES-H_2O emulsions, *oral presentation, 2017 AICHE Annual Meeting, October 29th – November 2nd, Minneapolis Convention Center, Minneapolis, MN, United States of America*

10. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Metal Ion Extraction with Hydrophobic Deep Eutectic Solvents, *oral presentation, Wetsus congres, October 9th – October 10th, De Harmonie, Leeuwarden, The Netherlands*

9. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *oral presentation, CHAINS 2016, December 6th – December 8th 2016, NH Conference Centre Koningshof, Veldhoven, The Netherlands*

8. Maaike C. Kroon, Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Marisa A.A. Rocha, Hydrophobic Deep Eutectic Solvents: Design, Properties and Applications, *oral presentation, Green Solvents Conference, October 6th – October 8th 2016, Halle 400, Kiel, Germany*

   (Invited lecture for professor Kroon)

7. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Dries Parmentier, Carin H.J.T. Dietz, Marisa A.A. Rocha, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents as water immiscible extractants: Design, Properties and Applications, *oral presentation, 26th EUCHEM on Molten Salts and Ionic Liquids, July 3rd – July 8th 2016, Conference Venue Hotel Savoyen, Wenen, Austria*

6. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents: Design, Properties and Applications, *oral presentation, 14th PPEPPD 2016, May 22nd – May 26th 2016, Hotel Solverde Spa & Wellness Center, Porto, Portugal*

   (The presentation was awarded to me, but only senior researchers were allowed to present work at this congress. Thus, professor Kroon presented it.)

5. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Marisa A.A. Rocha, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents: A New Generation of Water-Immiscible Extractants, *oral presentation, CHAINS 2015, November 30th – December 2nd 2015, NH Conference Centre Koningshof, Veldhoven, The Netherlands*

4. Dannie J.G.P. van Osch, Laura J.B.M. Kollau, Panos D. Kouris, Maaike C. Kroon, Processing of Lignin and the Removal of Detrimentals with Deep Eutectic Solvents, *oral presentation, European paper week 2015, November 17th – November 19th 2015, Thon Hotel EU, Brussels, Belgium*

3. Dannie J.G.P. van Osch, Laura J.B.M. Kollau, Maaike C. Kroon, Processing of Lignin and the Removal of Detrimentals with Deep Eutectic Solvents, *oral presentation, 6th Nordic Wood Biorefinery Conference, October 20th – October 22nd 2015, Scandic Marina Congress Center, Helsinki, Finland*

2. Dannie J.G.P. van Osch, Laura J.B.M. Kollau, Maaike C. Kroon, Pitch about the future use of deep eutectic solvents (DESs) in the paper industry, *pitch, European Paper Week 2014, November 25th – November 27th 2014, Thon Hotel EU, Brussels, Belgium*

1. Dannie J.G.P. van Osch, Laura J.B.M. Kollau, Maaike C. Kroon, Innovative methods for papermaking using Deep Eutectic Solvents, *oral presentation, European Paper Week 2014, November 25th – November 27th 2014, Thon Hotel EU, Brussels, Belgium*

Poster presentations at scientific conferences

12. Dannie J.G.P. van Osch, Marjorie G. du Pree Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, A Surfactant Based Deep Eutectic Solvents for the Production of DES in H_2O emulsions, *poster presentation, 27th Conference on Molten Salts and Ionic Liquids, October 7th – October 12th, Centro Cultural de Bélem, Lisbon, Portugal*

11. Dannie J.G.P. van Osch, Marjorie G. du Pree, Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, The Discovery of Novel Hydrophobic Deep Eutectic Solvent in Water Emulsions, *poster presentation, 27th Conference on Molten Salts and Ionic Liquids, October 7th – October 12th, Centro Cultural de Bélem, Lisbon, Portugal*

10. Dannie J.G.P. van Osch, Marjorie G. du Pree, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, The Discovery of Novel Hydrophobic Deep Eutectic Solvent in Water Emulsions, *poster presentation, International Symposium on Solubility Phenomena (ISSP 2018), July 15th – July 20th 2018, Hôtel Oceania l'Univers, Tours, France* (Best poster prize awarded to me by Springer)

9. Dannie J.G.P. van Osch, Marjorie G. du Pree Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, A Surfactant Based Deep Eutectic Solvents for the Production of DES in H_2O emulsions, *poster presentation, International Symposium on Solubility Phenomena (ISSP 2018), July 15th – July 20th 2018, Hôtel Oceania l'Univers, Tours, France*

8. Dannie J.G.P. van Osch, Marjorie G. du Pree Nicole M.W. van der Heijden, Jaap van Spronsen, A. Catarina C. Esteves, Remco Tuinier, Mark Vis, A Surfactant Based Deep Eutectic Solvent for the Production of DES in Water Emulsions, *poster presentation, 16th Conference of the International Association of Colloid and Interface Scientist (IACIS 2018), May 21st – May 25th 2018, Postillion Convention Centre WTC Rotterdam, Rotterdam, the Netherlands*

7. Dannie J.G.P. van Osch, Lawien Zubeir, Dries Parmentier, Adriaan van den Bruinhorst, Carin H.J.T. Dietz, Marisa A.A. Rocha, Nicole M.W. van der Heijden, Mark Vis, A. Catarina C. Esteves, Jaap van Spronsen, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents: Their Discovery and Design for Separations, *poster presentation, CHAINS 2017, December 5th – December 7th 2017, NH Conference Centre Koningshof, Veldhoven, The Netherlands*

6. Dannie J.G.P. van Osch, Lawien Zubeir, Dries Parmentier, Adriaan van den Bruinhorst, Carin H.J.T. Dietz, Marisa A.A. Rocha, Nicole M.W. van der Heijden, Mark Vis, A. Catarina C. Esteves, Jaap van Spronsen, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents: Their Discovery and Design for Separations, *poster presentation, 2017 AICHE Annual Meeting, October 29th – November 2nd 2017, Minneapolis Convention Center, Minneapolis, MN, United States of America*

5. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *poster presentation, CHAINS 2016, December 6th – December 8th 2016, NH Conference Centre Koningshof, Veldhoven, The Netherlands*

4. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents: A New Generation of Water-Immiscible Extractants, *poster presentation, 14th PPEPPD 2016, May 22nd - May 26th 2016, Hotel Solverde Spa & Wellness Center, Porto, Portugal*

3. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Marisa A.A. Rocha, Remco Tuinier, Maaike C. Kroon, Hydrophobic Deep Eutectic Solvents: A New Generation of Water-Immiscible Extractants, *poster presentation, CHAINS 2015, November 30th – December 2nd 2015, NH Conference Centre Koningshof, Veldhoven, The Netherlands*

2. Dannie J.G.P. van Osch, Maaike C. Kroon, The Use of Deep Eutectic Solvents (DESs) for the Recycling of Paper, *poster presentation, European Paper Week, November 25th - November 27th 2014, Thon Hotel EU, Brussels, Belgium*

1. Dannie J.G.P. van Osch, Maaike C. Kroon, The Use of Deep Eutectic Solvents (DESs) for the Recycling of Paper, *poster presentation NPS14, November 3rd - November 5th 2014, DeFabrique, Utrecht, Netherlands*

Non-scientific presentations and workshops

8. Hydrophobic Deep Eutectic Solvents: An Innovative Water-Immiscible Designer Solvent, *TedX pitch, June 5th 2018, Eindhoven University of Technology, Eindhoven*

7. Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Dries Parmentier, Carin H.J.T. Dietz, Marjorie G. du Pree, Nicole M.W. van der Heijden Jaap van Spronsen, Marisa A.A. Rocha, Maaike C. Kroon, Mark Vis, A. Catarina C. Esteves, Martin van Sint Annaland, Fausto Gallucci, Remco Tuinier, Design and Applications of Hydrophobic Deep Eutectic Solvents, *presentation for the 'Rotterdamsche Chemische Kring', April 9th 2018, Rotterdam*

6. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *presentation and workshop for high school students, March 12th 2018, Gymnasium Hagenum, Den Haag*

5. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *presentation and workshops in a study day for high school chemistry teachers and amanuenses, January 31st 2018, Eindhoven University of Technology, Eindhoven*

4. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *presentation and workshop for amanuenses, December 14th 2018, Wageningen University, Wageningen*

3. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *presentation and workshop for high school students, May 8th 2017, RSG Lingecollege, Tiel*

2. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *presentation and workshops in a study day for high school chemistry teachers and amanuenses, April 4th 2017, Radboud Pre-University College of Science, Nijmegen*

1. Dannie J.G.P. van Osch, Dries Parmentier, Carin H.J.T. Dietz, Adriaan van den Bruinhorst, Remco Tuinier, Maaike C. Kroon, Removal of Alkali and Transition Metal ions from Water with Hydrophobic Deep Eutectic Solvents, *presentation and workshop for high school students, February 16th 2017 Gymnasium Hagenum, Den Haag*

News articles based on my scientific work

4. An article in the 'Volkskrant' named 'Even stevig schudden, en al het vuil lost op'. (Link: https://www.volkskrant.nl/wetenschap/even-stevig-schudden-en-al-het-vuil-lost-op a4379086/)
3. Interview on NPO radio 1 in the show 'Nieuws en Co' on Friday 7 October 2016 at 16:20. (Link: https://www.nporadio1.nl/nieuws-en-co/onderwerpen/379323-oplosmiddel-voor-zware-metalen and https://www.youtube.com/watch?v=9iDFYcjCIdk)
2. Interview in C2W. (Link: http://www.c2w.nl/nieuws/eutectisch-oplosmiddel-vangt-zware-metalen/item18461)
1. Interview with Nemo kennislink. (Link: http://www.nemokennislink.nl/publicaties/nieuw-oplosmiddel-vangt-metalen)

Curriculum vitae

Dannie van Osch was born on 29-06-1990 in Geleen, the Netherlands. After finishing pre-university secondary education in 2008 at Trevianum Scholengroep in Sittard, he studied Chemical Engineering and Chemistry at the Eindhoven University of Technology (TU/e). In 2012 he graduated for his BSc degree within the group of Micro Flow Chemistry and Process Technology on the Claisen rearrangement under high temperature and pressure in a microreactor. In 2014 he graduated for his MSc degree within the group of Micro Flow Chemistry and Process Technology on the metal free photocatalytic perfluoroalkylation of pyrroles and indoles in microreactors and a study towards the distance-to-time transformation in microreactors. His BSc and MSc research were under the supervision of dr. Timothy Noël. During his MSc studies he also performed an industrial internship, in which he performed thermodynamic modeling of the NH_3-CO_2-H_2O system with the extended UNIQUAC model at Stamicarbon. He received his Master degree with the judicium cum laude.

In September 2014 he started a PhD project at TU/e, of which the results are presented in this dissertation. Initially, his supervision was by prof. dr. ir. Kroon and dr. van Spronsen, but after professor Kroon left TU/e it shifted towards prof. dr. ir. Tuinier, dr. Esteves and dr. van Spronsen.

The work on metal ion extraction removal from water with hydrophobic DESs gained widespread attention in the Dutch news, including an article in 'De Volkskrant' and an interview on NPO radio 1 in the show 'Nieuws en Co'. Next to presenting his work on scientific congresses, he also presented his work on multiple conferences for secondary school teachers and amanuenses and for high school students. Dannie has contributed to teaching thermodynamics (work classes and occasionally a lecture) for BSc students. During one year of his PhD he was in the board of the physical chemistry group, in which he represented the PhDs and Postdocs.

Acknowledgments

It is 13.30 on November 13th 2016, my father's 65th birthday, when I start writing my acknowledgments. The house is already crowded, but I can't stop thinking about the thing that is already haunting me for weeks; the acknowledgments of my thesis! The part of my thesis, which will (highly likely) be read the most. I did notice from quite some acknowledgments that they are written in the last weeks and thus contain some faults and/or mistakes such as miswritten names in quite the wrong context. For more information on this you can contact my paranimph and good friend Ivo. The main thing I want to avoid is forgetting people in my acknowledgments. Only thinking back on the last 2 years, I came across a lot of people who helped me with my research or helped me with becoming the person I am; hopefully a better person than before. I hope I will mention all of you, or else please forgive me if I have forgotten you.

First of all I would like to thank the people who made it possible that I could start and finish my PhD. Maaike, my gratitude for giving me a PhD position. It was most unfortunate that you left TU/e. I think we could have done much more interesting research together. Moreover, the Bio-Based Industries Joint Undertaking and the companies within Provides are acknowledged for their financial support. Gratitude goes to Annita Westenbroek for being the coordinator of the project. Moreover, special thanks to Robert Miller, Robert Hilbing and Math Jennekens for the close contact we had during the project.

While my PhD started with professor Kroon, it continued with professor Tuinier when Maaike left. Remco assembled, yes it is a word joke, a great team of scientist around me. Remco, gratitude for 'adopting' us when Maaike left. You gave me a chance to find my love for physical chemistry, of course with 'my babies', the hydrophobic deep eutectic solvents. Despite it was sometimes hard for me I enjoyed your critical look on science and the many debates we had about my work and science in general. Many thanks for the opportunities you gave me. I hope for you it was such a great time as it was for me. Catarina, despite our background is totally different, I loved to work together with you. I always have the idea that the projects I chose are high potential, but I try to keep them at a simple level. You always tackle the though problems, which I admire a lot. Moreover, I liked the conversations we had at some dinners when seated next to each other. The small compliments you gave about me as a scientist always meant a lot for me although I think you never realized that. A supervisor I had a great connection with, is Jaap van Spronsen. Jaap, what a blast did we have during our Friday conversations. Often they were about science, but I think at least 50% was not related to science. I always liked it when you said 'Dannie, you know what you have to do, just finish the thesis'. It gave me a lot of confidence. The 50% we didn't talk about science, you were a mentor to me during 2 years of my PhD. You taught me a great deal outside the field of science and I would truly like to thank you for that.

As a PhD defense should be, the show can only go on with a committee. Professor Hensen, I love the fact that you canceled other meetings for my defense. I am looking forward to my defense with you as the chairman. Catarina and Remco, as my 1^{st} and co-supervisor you helped me a lot, only a few more questions for me to answer to you, before I can finally call myself a doctor. Many thanks to the external members of my committee, professor Vlugt, Kegel and Aarts, to make the trip to Eindhoven for my defense. Also thanks to the two members from TU/e, dr. Noël and professor van Sint Annaland. I am looking forward to all your questions as my committee members and I am looking forward to celebrate this moment together with you.

Timothy Noël, a person I can write a book about. In my opinion a great scientist, but even more, one of my greatest and closest friends. Sometimes I wonder if you truly know what you mean to me, but also meant to me in my life. Since my BSc research you have been a mentor in my life and although you are extremely busy with your career, you always make time for me when I need a good conversation, that meant and means a lot to me! You always gave me a lot of confidence, for which I am still in debt to you. As your former PhD student Hannes mentioned, you are a catalyst for a group, but more important, a great mentor in life. Thank you for this Timothy, I can't wait to answer your questions during my defense. I feel honored that you are in my committee and I would like to thank Remco for giving me this chance.

Before continuing to thank all the people from the groups I worked in and my friends, some special thanks for the assistant professors, Mark Vis and Ivo Filot, that agreed to be my paranimphs. I hardly have problems with making decisions in my life, but choosing my paranimphs was a hard one. People like Carin, Adriaan, Bart, Ferdinand, Marco, you all passed my decision making, but I could only chose two. My apologies to you all! Mark, you are maybe at this point not yet an assistant professor, but I am sure you will become it in the near future! You are a very talented researcher, a great person to work with, but even more, a very good friend to me! I truly enjoyed working together with you. I wish you all the best in your scientific career and a great future together with Maartje. Ivo (JOAAAAA!!!), 'nutte Koempel', I feel honored that you are next to me during my PhD defense and that we can make a new memory together. So many things I can say to you and Sandra, but I think I already have mentioned all of them in my speech for Benthe. I wish you all the best in your scientific career and lots of happiness together with Sandra and your newly born, Benthe. Since I can't speech to myself regarding the Koempels, I presume it is your task this time. I am looking forward to your words about me!

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Almost at the end of my acknowledgements and I think she is already getting worried. Carin, I didn't forgot you! During the last 4 years I met quite some people that were special to me. You are absolutely one of them!!! You are that person that I can call during the night, a person that is always there for me. A person with good advice, always time for me and a person that keeps me with my feet on the ground. You are one of these people I could have not done this without. For all the times you helped me in the field of science or in my social life, I am in debt for life. I wish all the best and lots of success to you, Rene, Guido and Fabiènne.

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To wrap up 10 years at Eindhoven University of Technology, of which 4 years as a PhD, the final words of my thesis! All good things come to an end. I already thought a lot of what I should mention in this final paragraph. I have a lot of emotions, but one overcomes all of them. I feel sad. My life at Eindhoven University of Technology is coming to an end, and I am seriously going to miss it. I worked hard but also enjoyed social time after working hours doing sports or drinking beer in the F.O.R.T., always with people that I have the privilege to call my friends. The time is here now, 'this is the end'. Goodbye Eindhoven, goodbye my beloved faculty of chemical engineering and chemistry, goodbye SPC, goodbye friends. I will miss you, but as once said in a movie about the future 'I will be back'. To the people that I had to acknowledge, but I forgot, my sincere apologies. It was quite a task to remember all of you, despite this was the first chapter I started writing on.