INVESTIGATION OF DEEP EUTECTIC SOLVENTS AS A REACTION
MEDIUM FOR METAL CHLORIDE BASED CHEMICAL HEAT PUMPS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

EZGİ GÖZDE

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMİCAL ENGİNEERİNG

SEPTEMBER 2019

Approval of the thesis:

INVESTIGATION OF DEEP EUTECTIC SOLVENTS AS A REACTION MEDIUM FOR METAL CHLORIDE BASED CHEMICAL HEAT PUMPS

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ABSTRACT

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September 2019, 76 pages

Metal chlorides can react with gas phase ammonia and form complex compounds. Due to reversibility and high heat of reaction, these ionic reactions are attractive for the application of chemical heat pumps which can provide the ability to capture the rejected low-grade heat and to reuse it at increased temperature levels. The pressure and temperature interval of ammonia sorption into $CaCl_2$ is suitable for heat upgrade of waste heat streams, geothermal energy and solar energy sources. However, heat and mass transfer limitation of the gas-solid phase is one of the major challenges. In order to overcome this challenge, in this thesis, the potential usage of the deep eutectic solvents(DES) as a reaction medium for the $CaCl_2$-NH_3 pair was studied. As DES, in different molar ratios, $ZnCl_2$-urea and ChCl-urea pairs were synthesized. From stability tests, it was found that $ZnCl_2$-urea DES which has a maximum 30 days of a lifetime is significantly less stable than ChCl-urea DES which has a lifetime more than 6 months under ambient conditions. The solubilities of $CaCl_2$ were determined as 3.7wt% and 5.3wt% for the $ZnCl_2$-urea molar ratio of 3.5:10 and 2.5:10 respectively. Ammonia sorption experiments revealed that higher amount of ammonia is absorbed into $CaCl_2$-$ZnCl_2$-urea suspension than pure solid $CaCl_2$. Ammonia sorption takes place with a significant rate and extend in $CaCl_2$-ChCl-urea DES but much slower

than the one observed for $CaCl_2/ZnCl_2$-urea samples. The desorption pressure-temperature equilibrium relationship exhibit more complex trend than the linear Clausius-Clapeyron equation because of the complex nature of sorption into $CaCl_2/ZnCl_2$-Urea mixture.

Keywords: Deep Eutectic Solvents, Solubility of a Salt in DES, Chemical Heat Pumps

ÖZ

DERİN ÖTEKTİK ÇÖZÜCÜLERİN METAL KLORÜR BAZLI KİMYASAL ISI POMPALARINDA KULLANIMININ İNCELENMESİ

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Eylül 2019, 76 sayfa

Metal klorürler gaz fazındaki amonyak ile tepkimeye girerek kompleks yapılar oluşturabilir. Bu reaksiyonlar, tersinir ve yüksek reaksiyon entalpilerinden dolayı kimyasal ısı pompası uygulamaları için tercih edilmektedir. Kimyasal ısı pompaları, düşük sıcaklıktaki ısıyı yüksek sıcaklıkta tekrar kullanılabilir ısıya dönüştürme özelliği nedeniyle birçok endüstriyel proseste tercih edilmektedir. $CaCl_2$'e amonyak sorpsiyonun basınç ve sıcaklık aralığı, atık ısının, jeotermal enerji ve güneş enerjisi kaynaklarının kullanılabilir ısıya çevrilmesi için uygundur. Ancak, sıvı-gaz fazının ısı ve kütle transfer katsayıları düşük olması endüstriyel uygulamalardaki güçlüklerden biridir. Bu sorunun aşılması amaçlanarak, bu tezde, derin ötektik çözücülerin (DES) $CaCl_2-NH_3$ çifti için olası reaksiyon ortamı olarak kullanılması çalışılmıştır. Derin ötektik çözücü olarak farklı molar oranlarda $ZnCl_2$-üre ve ChCl-üre sentezlenmiştir. Stabilite testlerinden elde edilen sonuçlarda, oda şartlarında 30 gün raf ömrüne sahip $ZnCl_2$-Üre DES'inin, 6 aydan daha uzun raf ömrüne sahip ChCl-Üre DES'inden çok daha az stabil olduğu tespit edilmiştir. $CaCl_2$'ün çözünürlüğü, 3.5:10 $ZnCl_2$-üre molar oranında kütlece %3.7, 2.5:10 $ZnCl_2$-üre molar oranında ise kütlece %5.3 olarak ölçülmüştür. Amonyak sorpsiyon deneylerinde, $CaCl_2-ZnCl_2$-Üre süspansiyonunun, saf $CaCl_2$'e göre daha fazla amonyak absorbe ettiği gözlenmiştir. Amonyak

sorpsiyonu, CaCl$_2$-ChCl-Üre süspansionunda belli bir oranda saptanmış ancak CaCl$_2$-ZnCl$_2$-Üre süspansiyonunda gözlenenden daha yavaştır. CaCl$_2$/ZnCl$_2$-Üre süspansiyonuna sorpsiyon prosesinin kompleks yapısından dolayı, desorpsiyon basınç-sıcaklık denge ilişkisi doğrusal Clausius-Clapeyron denkleminden daha karmaşık bir trend sergilemiştir. Sorpsiyon dengesinin doğrusal olmayan yapısı NH$_3$ desorpsiyonunun CaCl$_2$, ZnCl$_2$ ve DES çözeltisinde de gerçekleşmesiyle açıklanabilir.

Anahtar Kelimeler: Derin Ötektik Sıvı, Tuzun DES'teki Çözünürlüğü, Kimyasal Isı Pompası

To my parents,

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

DES	Deep Eutectic Solvent
DESs	Deep Eutectic Solvents
IL	Ionic liquid
ILs	Ionic Liquids
ΔT_f	Freezing Point Difference
Mg	Milligram
°C	Degree Centigrade
%	Percentage
cm^{-1}	Per centimeter
g	Gram
ml	milliliter
e.g.	For example
mm	Millimeter
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HBDs	Hydrogen Bond Donors
U	Urea
$ZnCl_2$	Zinc Chloride
ChCl	Choline Chloride
$CaCl_2$	Calcium Chloride
NH_3	Ammonia
N_2	Nitrogen
HF	Hydrofluoric Acid
T_f	Freezing Temperature
T_m	Melting Temperature
T_g	Glass Transition Temperature
FTIR	Fourier Transform Infrared Spectroscopy
ICP	Inductively Coupled Plasma
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
Pa	Pascal
s	second
Wt %	Percentage by Weight
VOC	Volatile Organic Carbon
COP	Coefficient of Performance

CHAPTER 1

INTRODUCTION

Metal chlorides such as $CaCl_2$, $MgCl_2$, $MnCl_2$ and $BaCl_2$ react with gas-phase ammonia forming the complex compounds, $MCl_2 \cdot xNH_3$ ($2 \leq x \leq 8$). Due to reversibility and high heat of reaction, these ionic reactions are attractive for the applications of chemical heat pumps, ammonia storage, and ammonia adsorption. However, low thermal conductivity of solid phase, gas-solid mass transfer limitations and dimensional inconsistency of solid-phase are the major challenges that need to be overcome. In order to improve the heat and mass transfer, suspending metal chloride in a solvent (gas-liquid-solid) is one possibility, but a better solution is to dissolve metal chlorides in a solvent and perform the reaction in gas-liquid phase. The best solvent for these organic metal chlorides is water which is not suitable for this approach at all because of the reaction of metal chlorides with water which forms hydrides ($MgCl_2 \cdot xH_2O$). Therefore, there is a need for solvents for metal chlorides.

Deep eutectic solvents (DES) are environmentally friendly solvents having unique properties such as low vapor pressure, low toxicity and low flammability, etc. High solubility of metal salts in deep eutectic solvents make them very attractive for being used in electrochemical plating, metal polishing, and metal extraction industry. The aim of this work is to investigate the potential of the usage of Deep Eutectic Solvents (DESs) in chemical heat pumps as a solvent and reaction medium which is useful for dissolving metal chlorides in order to enhance reaction rates, to facilitate the transport of solid materials, to provide a heat sink during highly exothermic reactions and to allow absorption of ammonia.

In this study, the ammonia absorption into the solution of $CaCl_2$ in zinc chloride ($ZnCl_2$)-urea and choline chloride (ChCl)–urea deep eutectic solvents were

investigated. In addition, the solubility of $CaCl_2$ in $ZnCl_2$-urea and ChCl-urea at room temperature were determined.

1.1. Brief Introduction of Ionic Liquids (ILs)

Ionic liquids are a class of fluids that consists of ions and they are liquid at temperatures below 100°C [1]. The most widely used ionic liquids are classified into two subcategories. One of them is formed from metal halides and organic salts, and the other one contains discrete anions. Ionic liquids are also considered as green solvents because of their recyclability potential and nonhazardous content. They have the potential to be highly versatile solvents with properties that can be easily tuned for specific uses. Ionic liquids can be considered as the ancestor of deep eutectic solvents.

1.2. Deep Eutectic Solvents

Deep eutectic solvents (DESs) are classified as a new class of green ionic solvents because of their properties such as low vapor pressure, low toxicity, low flammability, benign nature of the components forming the solvent and low cost. Therefore, due to the increasing demand for eco-friendly and sustainable processes, application areas of deep eutectic solvents continuously increase [2]. Ionic liquids contain one discrete anion and cation, while deep eutectic solvents contain eutectic mixtures of Lewis or Brønsted acids and bases which have a variety of anionic and cationic species. [3] DESs and ionic liquids have similar physical properties but DESs are generally more preferable than ionic liquids because of their low cost, nontoxicity of the ingredients and preparation methods.

1.2.1. Types of Deep Eutectic Solvents

There are so many possible combinations of hydrogen bond donor and hydrogen bond acceptor that can form a eutectic mixture. DESs are broadly classified into four types. These four types of DESs differ from each other with respect to the type of hydrogen bond acceptor and donor which are given in the Table 1.1

Table 1.1. *General Formula Classification of DES [3]*

Type	Definition	Formula	Terms	Examples
I	Quarternary salt and metal halide	$Cat^+X^- + zMCl_x$	M = Zn, Sn, Fe, Al, Ga, In	$ChCl + ZnCl_2$
II	Quarternary salt and hydrated metal halide	$Cat^+X^- + zMCl_x.yH_2O$	M = Cr, Co, Cu, Ni, Fe	$ChCl + CoCl_2 \ .6H_2O$
III	Quarternary salt and hydrogen bond donor	$Cat^+X^- + zRZ$	Z =$CONH_2$, COOH, OH	ChCl + Urea
IV	Metal halide and hydrogen bond donor	$MCl_X + zRZ$	M=Al, Zn and Z=$CONH_2$,OH	$ZnCl_2$ + Urea

In this study Type I, Type III and Type IV DESs were synthesized because of their components are nontoxic, available, inexpensive and the solvents are easy to prepare. Besides, they are good candidates for applications in chemical heat pumps because of these properties and they are generally good reaction media.

1.2.2. Eutectic Point

The word "eutectic" is in Greek, and it means: "can be melt easily". The eutectic point, as illustrated in Figure 1.1, is the lowest temperature that the solution solidifies. [4]. Because of the interaction forces between the two components which is generally hydrogen bonding, the freezing point depression occurs. In deep eutectic solvents, two different solids are mixed at certain ratios, and as a result, the solution attains a much

lower melting point than the melting points of both components. The ratio of the components has a crucial role on the freezing point of the solvent [5].
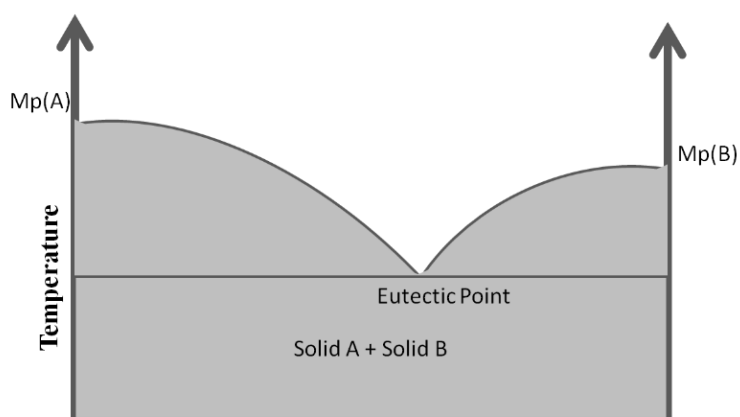
Figure 1.1. Eutectic point of two component Deep Eutectic solvents

Abbott et al. first described the deep eutectic solvent phenomenon with ChCl (choline chloride) and urea in 1:2 molar ratio in 2003 [6]. It was a type III DES and ChCl was a quarternary salt (hydrogen bond acceptor) and urea acts as a hydrogen bond donor which have melting point of 302°C and 133°C respectively. In this mixture, the freezing point depression was found as 178°C where the eutectic point was 12°C. The reason for the huge decrease in the freezing point of the mixture relative to the melting points of the individual components is the charge delocalization occurring through the hydrogen bonding. [7]

The hydrogen bond donating group interacts with the anion of quaternary salt and increases its effective size. Therefore, the interaction with the cation decreases and it reduces the freezing point of the mixture. The freezing point of any mixture containing a quaternary salt and a hydrogen bond donor is dependent on two major factors. The first one is the individual lattice energies of both quaternary salt and hydrogen bond donor. The second one is the degree of interaction between the anion of the quaternary salt and the hydrogen bond donating group. If the anion-hydrogen bond donor interaction is strong, the entropy of the system increases, thereby lowering the freezing point of the system.[7]

In the literature, there are some studies on which Type I DES components can form eutectic in ambient conditions. It was observed that to be able to form an eutectic mixture in ambient temperature metal halides generally have a melting point of more than 250°C [1]. The examples of such eutectic mixtures are those with $FeCl_3$ which have a melting point of 308°C can form eutectic mixture with 1-butyl-3methylimidazolium chloride, and $SnCl_2$ which have eutectic point of 247°C can form eutectic mixture with Choline Chloride [8].

Moreover, for the Type II deep eutectic solvents, it was observed that the metal halide components generally have lower melting point than the salt component [1]. Table 1.2 lists the components of the most common deep eutectic solvents and the eutectic melting temperatures with their molar ratios. As it can be seen from the table, the freezing point of each solvent is smaller than the melting points of its components.

Table 1.2. *Freezing points of DES and its components*

Hydrogen Bond Acceptor	Melting Point (^0C)	Hydrogen Bond Donor	Melting Point (^0C)	Molar Ratio (HBA:HBD)	Freezing Point of DES (^0C)	Ref.
ChCl	303	Urea	133	1:2	12	[6]
$ZnCl_2$	293	Urea	134	1:3.5	9	[9]
ChCl	303	Glycerol	17.8	1:2	-40	[6]
ChCl	303	Thiourea	175	1:2	69	[10]
$ZnCl_2$	293	Ethylene Glycol	-12.9	1:3	-30	[9]
$ZnCl_2$	293	Hexanediol	42	1:4	-23	[9]

Methyltriphenyl phosphonium Bromide	232	Glycerol	17.8	1:5	-4.03	[11]
Methyltriphenyl phosphonium Bromide	232	Ethylene glycol	-12.9	1:5	-49.34	[11]
Methyltriphenyl phosphonium Chloride	346	Glycerol	17.8	1:5	50.36	[11]
Methyltriphenyl phosphonium Chloride	346	Ethylene glycol	-12.9	1:5	47.91	[11]

1.2.3. Properties of Deep Eutectic Solvents (DESs)

The potential use of a solvent in chemical and industrial processes depends on the properties such as vapor pressure, density, viscosity, refractive index, toxicity, hardness, pH, surface tension, conductivity, polarity, miscibility, etc. From this perspective, the properties of DESs have a crucial role on its performance. In literature, there are many studies on DESs' properties and how these properties can be tuned for better performance. For deep eutectic solvents, most commonly reported physical properties are density and viscosity since they are the major properties determining the applicability of DES in mass transfer operations in chemical processes [12].

1.2.3.1. Density

Density is a very essential physical property of DESs in chemical heat pumps in order to estimate the size and the cost of the system. Density relies on the presence of vacancies in the DES network [13]. The density of deep eutectic solvents is directly related to the molar ratio, molecular organization, and packing of the components that are forming the deep eutectic solvent. Generally, they have higher densities than that of water [14]. For instance, type IV $ZnCl_2$–HBD eutectic mixtures have densities higher than 1.3 g/cm^3 [12]. Studies show that densities of DES are higher than the pure

HBA and pure HBD. This may be explained with the hole theory, when DES constituents are mixed average hole radius decreases by increasing density. Mjalli et al. suggested a model to find the density of deep eutectic solvents at different temperatures. [15]. In the study, they studied with three different salts (Choline Chloride, diethyl ethanol ammonium chloride and methyl triphenyl phosphonium bromide) and three different hydrogen bond donors (glycerol, ethylene glycol and trifluoroacetamine). They have modified the racket equation and their model for the density calculation of DES is as follows [16] [17].

$$\rho_L = \left(0.01256 + \frac{0.9533M}{V_c}\right)\left[\left(\frac{0.0039}{M} + \frac{0.298}{V_c}\right)V_c^{1.033}\right]^a$$

$$a = -\left[\frac{1-T_f}{1-T_b}\right]^{2/7} \hspace{3cm} \text{Equation 1}$$

Where ρ_L is the density of DES, V_c is the critical volume, M is the molecular weight, T_f is the reduced temperature and T_{br} is the reduced temperature at normal boiling point.

The organic salt/HBD molar ratio also has an obvious effect on the densities of DES. Abbott et al. studied ChCl-Glycerol DES systems and found that as the molar content of ChCl increased from 5 % to 35 %, the density of DES varied from 1.26 to 1.18 g/cm^3 [18].

1.2.3.2. Viscosity

Viscosity is an important parameter in mass and heat transfer operations. For the potential applications of DESs, generally low viscosities of DESs is highly desirable. The viscosity of DES is critical in this study because the solvent used in chemical heat pumps is aimed to increase mass and heat transfer. In general, deep eutectic solvents have viscosities higher than 100 cP, and therefore, can be referred as high-viscosity solvents at room temperature, which limits their applications. The hydrogen-bond network between each component, the large ion sizes, small void volumes and some electrostatic or van der Waals interactions lead to high viscosities [12].

There is a huge effort to understand and predict the fluid properties of DESs [19]. The high viscosity of DESs is often attributed to the presence of an extensive hydrogen bond network between each component, which results in a lower mobility of free species within the DES [12]. In general, viscosities of DESs are mainly affected by the chemical nature of the DES components (type of the ammonium salts and HBDs, organic salt/HBD molar ratio, etc.), the temperature, the water content and free volume. Capper et al., used the hole theory to explain the fluid behavior of DES [20]. According to studies, the viscosity of a fluid is related to the free volume and the probability of finding holes of suitable dimensions for the solvent molecules/ ions to move into [21].

In table 1.3 the densities and the viscosities of some common deep eutectic solvents which is used in this study are given.

Table 1.3. *Densities and Viscosities of some common DES*

Halide Salt	Molecular precursor	Molar Ratio of Salt to hydrogen bond donor (mol :mol)	Density (g/cm^3)	Viscosity at 20° C (cP)
ChCl	Urea	1 : 2	1.206	750
$ZnCl_2$	Urea	1 : 3.5	1.63	11300
ChCl	Glycerol	1 : 2	1.18	376

1.2.4. Stability of Deep Eutectic Solvents

In literature there are various studies on the stability of DES were some works on stability of DES. Lifetime of a solvent is referred as stability time. Lian et. al studied on zinc chloride and urea mixtures in different molar ratios and they have reported the lifetime as the time at which the first solid crystal within the liquid was observed. Their results are given in Table 1.4 [22].

Table 1.4. Lifetimes of $ZnCl_2$-urea DES

Molar Ratio ($ZnCl_2$: urea)	Lifetime
2 : 10	1 hour
2.5 : 10	1 day
3 : 10	30 day
3.5 : 10	10 day
4 : 10	7 day
4.5 : 10	3 day

Besides the lifetime of DES, there are some studies on the thermal stability of DES. In these studies, TGA is the most commonly used technique to investigate the thermal stability. Haz et al. studied the thermal stability of ChCl-citric acid in the temperature range 25°C-400°C and they have reported that this DES is thermally stable up to 155°C [23]. In addition, Chen et al. reported the TGA curve for ChCl-urea DES under different heating rates and found that DES start to decompose around 150°C [24].

1.2.5. Preparation Methods of Deep Eutectic Solvents

In the preparation of DES, the components should be pure. If they were not, the first preparation step should be purification in order to increase the efficiency and get rid of unwanted side products. In addition, the purity of the components determines the purity of DES. The next preparation step is mixing. DES are prepared by mixing a hydrogen bond donor and hydrogen bond acceptor. The mixing can have two different kinds. One of them is to mix the two components and raise the temperature the other method is to first melt the lower melting point temperature component then added the higher melting temperature compound.

1.2.6. Applications of Deep Eutectic Solvents (DES)

DESs have recently received a great interest in diverse fields. Growing number of studies have been reported in literature on the applications of DESs in polymer synthesis[25], carbon-carbon nanotube composite preparation[26], biodiesel purification[27], fabrication on metal surfaces, coatings[28], bulk processing of metals[29], synthesis of nanoparticles and electrochemical applications [30] etc.

One common application area of deep eutectic solvents is the use as reaction media such as inorganic material synthesis. Boston et al. studied the synthesis of barium titanate by using choline chloride-malonic acid DES, which offers several advantages over the traditional solid-state route[31]. By using the deep eutectic solvent, they reduced the synthesis time by eliminating the multiple processing routes as well as a calcination step, which reduced the energy consumption. Abbott et al. reported that metal oxides are generally soluble in choline chloride based DES including ethaline (ethylene glycol-choline chloride), maline (malonic acid-choline chloride) and reline (urea-choline chloride) [14]. The metal ions forming complexes with the chloride anions lead to the dissolution of the metal oxides in DES and formation of the metal oxide-DES solutions. Ionothermal synthesis of various inorganic materials in deep eutectic solvents were also studied [32]. Nanostructured nickel compounds and surface-modified silica particles are among the inorganic materials synthesized in reline. Nickel phosphide nanoparticles and nickel oxide nanostructured films were synthesized in ethaline, and iron (III) hexacyanoferrate nanospheres were synthesized in maline. [33] Meanwhile DES based on choline chloride and urea was used in the production of aluminum phosphates [34]. The urea in the solvent decomposes during the reaction, and therefore, it provides a template for the product. DES have been also used as an extraction media for the extraction of hydroxybenzoic acid, apigenin, vanillic acid, etc [19]. Zeng et al. also worked with DES as a novel extraction media for protein partitioning [35]. Due to the benign natures of DES components, these solvents can also be used in biological and biomedical applications. The potential of DESs as possible anti-cancer agents was assessed in a recent toxicology study. Hayyan

et al. [36]determined the IC50 values of different ammonium-based DESs on several cancer cell lines. They have found that the cytotoxicity and selectivity of in vitro and vivo cells can be influenced by the composition of DES by varying the salt/HBD combination and molar ratio. Other applications of DES include electroplating, metal electro decomposition, metal extraction and the processing of metal oxides [37].

1.3. Heat Pumps

Utilization of fossil fuels and energy conversion cycles produce a significant amount of useless low-grade heat which is generally released into the atmosphere. Waste heat is about 30% to 50% of the total energy input of the thermal conversion processes. Therefore, waste heat recovery or conversion processes are very beneficial to reduce greenhouse gas emissions, fuel economy, and energy efficiency. Waste heat conversion could be performed by heat pumps. Heat pumps can be used to upgrade or transform the waste heat from lower temperatures to high temperatures or to utilize waste heat for heating-cooling operations such as refrigeration, air conditioning, etc. [38]. Chemical heat pumps are promising thermal energy conversion processes which depends on the heat of absorption/sorption of gases or vapors over adsorbents. Therefore, low-grade heat can be used as a heating or cooling medium to drive adsorption/desorption reaction instead of electrically driven vapor compressors.

1.3.1. Chemical Heat Pumps

Chemical Heat Pumps (CHP) are receiving growing interest in research to improve the utilization of low temperature energy sources such as waste heat emissions, solar and geothermal energy with higher efficiency. Chemical heat pumps do not include moving parts like compressors. They have lower number of process components and do not emit combustible or harmful gases to the environment and they are more suitable to batch operations. Therefore, chemical heat pumps are more advantageous than the traditional heat pump systems[37]. In accordance with the above-mentioned advantages, there are many studies on zeolite-water, silica gel-water, active carbon-

methanol adsorption systems[39]. Some heat pump products were commercialized especially for cooling and refrigeration applications[40]. However, there are some tradeoffs in the transformation of waste heat or the low temperature heat source (such as geothermal energy at 60-90°C) to higher temperatures 175-250°C at which the energy is more useful such as steam that should be heated to drive a turbine. In these temperature bands, water-zeolite based systems are not helpful and metal salt-ammonia or metal-H_2 pairs can be considered [40]. $CaCl_2$, $NiCl_2$, $BaCl_2$, $SrCl_2$ salts, adsorption desorption reversible relations with ammonia occurs at 20-300°C and 0.1-15 atm. [41][42][43]. Wang et al. studied the $CaCl_2$ ammonia heat pump that can be an example for both adsorption and chemical heat pumps[44].

1.3.1.1. Systems of Chemical Heat Pumps

Chemical heat pumps can provide the ability to capture the rejected low-grade heat and enables the use of it at elevated temperatures, and therefore, can be preferable in various industrial processes[38]. Different from the vapor compression heat pump, chemical heat pump systems comprised of an evaporator, a condenser, an adsorption reactor and a desorption reactor[45]. Chemical heat pumps do not include a compressor but they include reactors providing the reaction energy, thus they are referred to be more economical than the vapor compression heat pumps. In addition, they are classified as more environmentally friendly because they eliminate the uses of hazardous refrigerants.

In a chemical heat pump, exothermic sorption and endothermic desorption reactions take place in the reactors [37]; in some cases, one reactor can be used for consecutive processes of sorption and desorption[46]. Its working principle mainly depends on the ability to store energy in the reversible reactions, through in which they upgrade the low-grade heat. There are two types of chemical heat pumps, which are one-salt and two-salt systems.
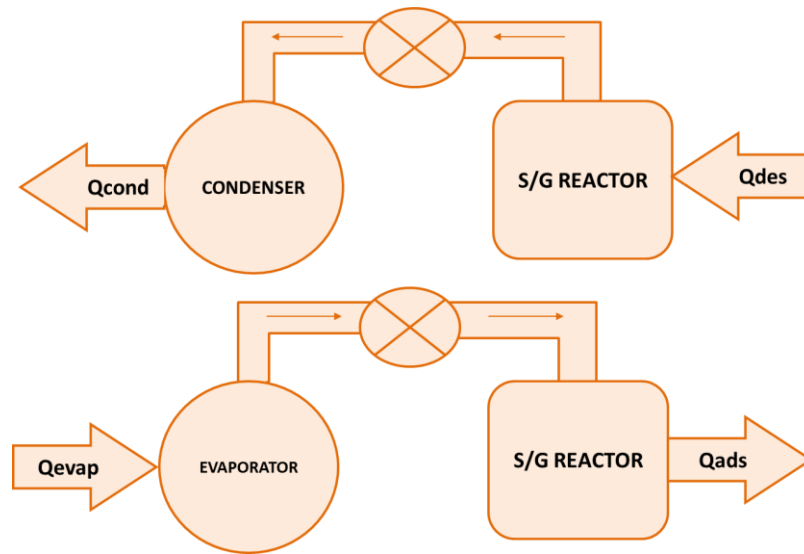
Figure 1.2. Schematic diagram of a chemical heat pump with one salt.

One-salt sorption chemical heat pumps (Fig. 1.2) are batch systems with a single sorption and single desorption processes. Calcium chloride-ammonia pair is the most commonly studied sorbent-sorbate pair in one-salt systems [35]. In the desorption phase, the system is heated by an external heat source, and the desorption of the sorbate occurs, which the vapor is transferred to the condenser, and pressurized in which its phase changes from vapor to liquid, ejecting heat to the surroundings. During the adsorption phase, liquid sorbate is firstly evaporated in the evaporator by using heat provided from an external heat source. The vapor sorbate is then transferred to the reactor, by sorption during which heat is released as upgraded heat providing thermal energy to the end-user.
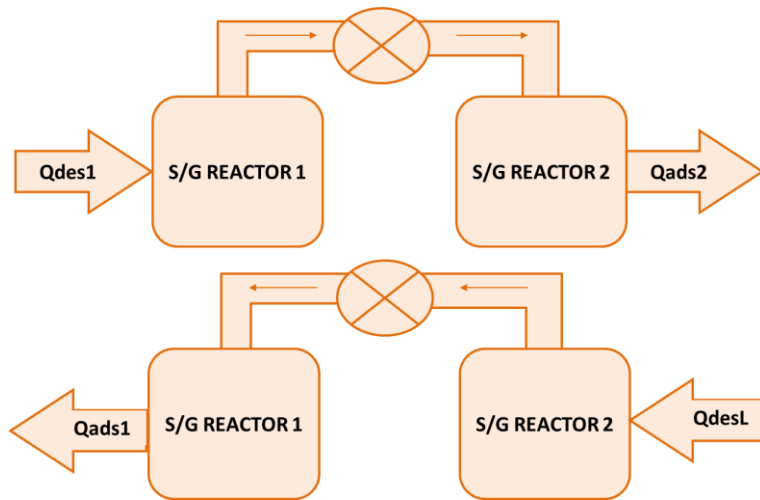
Figure 1.3. Chemical Heat Pump with two salt [35]

In a two-salt chemical heat pump, condenser and evaporator are replaced with a second pair of sorption and desorption reactors that uses a different sorbent than the first pair of reactors (Figure 1.3). Under the same working pressure, the salt which reacts at lower temperature is called as the low-temperature salt, while the other is referred as the high-temperature salt. Since in a two-salt system, heat is consumed for the desorption of the low-temperature sorbate rather than the vaporization of ammonia, the theoretical cooling capacity of the two salt systems are relatively higher than the one-salt chemical heat pumps since the energy requirement of the prior process is greater than the latter [35].

1.3.1.2. CaCl$_2$-Ammonia pair in Chemical Heat Pumps

The reversible sorption reactions of calcium chloride-ammonia pairs are given in the following equations [47].

$$CaCl_2(s) + NH_3(g) \leftrightarrow CaCl_2 \cdot NH_3(s) \qquad\qquad \text{Rxn 1}$$

$$CaCl_2 \cdot NH_3(s) + NH_3(g) \leftrightarrow CaCl_2 \cdot 2NH_3(s) \qquad\qquad \text{Rxn 2}$$

$$CaCl_2 \cdot 2NH_3(s) + 2NH_3(g) \leftrightarrow CaCl_2 \cdot 4NH_3(s) \qquad\qquad \text{Rxn 3}$$

$$CaCl_2 \cdot 4NH_3(s) + 4NH_3(g) \leftrightarrow CaCl_2 \cdot 8NH_3(s) \qquad\qquad \text{Rxn 4}$$
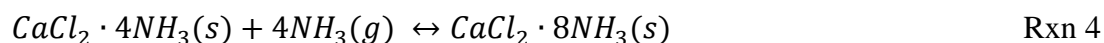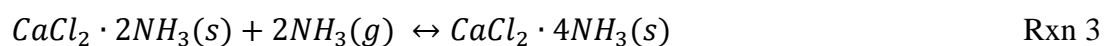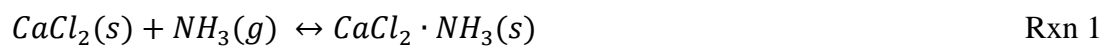
Heat of reactions are -45.5kJ/mol, -42.1 kJ/mol, -40.9 kJ/mol, and -39.6 kJ/mol for the reactions 1,2,3 and 4, respectively. Temperature and pressures of the reaction conditions affect the stoichiometry of ammoniates. At atmospheric pressure and 25°C, maximum two moles of ammonia is sorbed with one mole of calcium chloride[47].

Critoph et al. studied the performance of $CaCl_2$ reactor for the application in ammonia-salt based thermal transformers [48]. They have reported entropy and enthalpy of the reactions which is based on the assumptions of Clausius Clapeyron equation. The results are presented in Table 1.5.

Table 1.5. *Entropy and enthalpy values for the formation of CaCl₂ (2-4)NH₃ and CaCl₂ (4-8)NH₃* [48]

	ΔH (J.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
$CaCl_2(2-4)NH_3$	42100	134.1
$CaCl_2(4-8)NH_3$	42100	139.0

1.3.2. Efficiency of a Heat Pump

For the efficiency, a term COP is used in heat pumps[49]. The conventional heat pumps perform cooling effect as the adsorbate boils due to low pressure at the evaporator side and the energy input supplied to the adsorbent bed during desorption of the adsorbate for regeneration of the system. The equation of THE COP is given in Equation 2. This equation is used in choosing the adsorbate material[50].

$$COP = \frac{latent\ heat\ of\ adsorbate}{heat\ of\ desorption}$$
Equation 2

The coefficient of performance of an ideal heat pump can be defined as given in Equation 3 [51].

$$COP_{ideal} = \frac{2\Delta H_{vap}}{\Delta H_{rxn}} = \frac{T_{desorption}}{(T_{desorption} - T_{adsorption})}$$
Equation 3

However, the actual efficiency is directly related to heat transfer that occurred between hot and cold fluids and the amount of energy that is required for heating/cooling of solid sorbent[52].

In Figure 1.2., the power of chemical heat pump depends on the amount of the sorbent and adsorbent used in absorption and desorption, the amount of ammonia that is adsorbed or desorbed and the duration of absorption-desorption cycles. In literature, experimental results show that the actual COP values can reach only half of the ideal COP values[35]. According to experimental results, COP values are between 0.35 and 0.6 whereas the ideal COP values are calculated in the range of 0.95 and 1 [37][53]. The biggest obstacle in the commercialization of chemical heat pump is their low COP values than expected[37].

1.3.2.1. Factors Affecting Efficiency of a Chemical Heat Pump

There are so many factors that can affect the efficiency of a chemical heat pump but the main factors are thermo-physical properties of a material pair, operating pressure-temperature, adsorption bed geometry and physical properties of the sorbent.

In the design of a heat pump, the choice of sorption pair is important. As COP is concerned, in order to have the highest COP, it is important to keep the heat of sorption as low as possible and the latent heat of the sorbate as high as possible. Latent heat is a function of sorbate type, operating pressure, and cooling temperature, while the heat of sorption is a function of sorbate-sorbent pair, operating pressure and desorption temperature. Therefore, selecting different pairs directly affect the COP of the heat pump. In addition, the choice of sorbate sorbent pair also determines the operating pressure and temperature. In the sorption systems, the pressure of vapor is an important factor that affects the capacity and the rate of the reaction. The partial pressure of the vapor inside the system is limited to the vapor pressure of the sorbate at the cooling temperature.

1.3.3. Clausius Clapeyron Equation for Heat Pumps

The ammonia liquid-vapor equilibrium and calcium chloride salt-ammonia complex's equilibrium pressure can be explained with the well-established Clausius-Clapeyron equation. The Clausius-Clapeyron equation is given in Equation 4 where ΔHrxn and ΔS are the changes of enthalpy and entropy respectively. [54]

$$\ln(Peq) = \frac{-\Delta Hrxn}{RT} + \frac{\Delta S}{R} \qquad\qquad \text{Equation 4}$$

The operation principle of a chemical heat pump is depicted in Figure 1.4. As it can be seen from the figure, an external heat is supplied to the evaporator and the process starts with the evaporation of ammonia which is in low pressure and low temperature. The equilibrium line in the left hand side represents the Clausius-Clapeyron equation for the vapor-liquid equilibrium line of ammonia. Similarly, the equilibrium line in the right hand side represents the Clausius-Clapeyron equation for the equilibrium of salt-ammonia complex with ammonia vapor. Ammonia vapor reacts with metal salt and gives heat. To complete the cycle, metal salt-ammonia complex is heated and desorption of ammonia occurs. The desorbed ammonia's pressure is increased, ammonia condenses and sends to the evaporator.
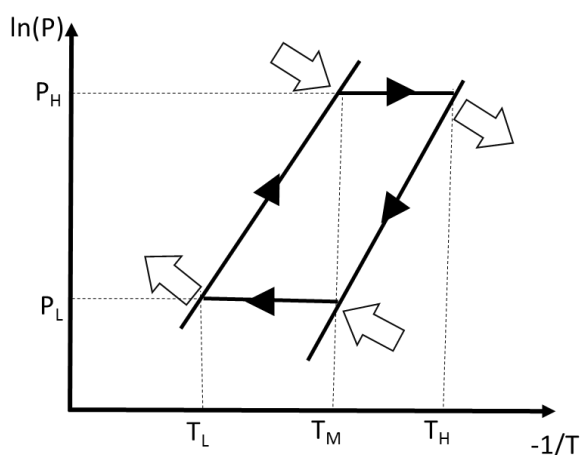
Figure 1.4. Clausius-Clapeyron diagram for Chemical Heat Pumps

1.4. Problems in Chemical Heat Pumps

In chemical heat pumps, the usage of solid-gas systems has some challenges that need to overcome. The major drawbacks are; low thermal conductivity of solid phase, gas-solid mass transfer limitations and dimensional inconsistency of solid phase. The commonly used metal salt-ammonia reactions used in chemical heat pumps are reversible reactions, therefore the net reaction rate is limited with the kinetic and thermal effects. Mass transfer, diffusion resistance within the material [55]. In solid salt-ammonia systems, the heat evolves because of the adsorption reaction. This heat should be removed from the system without causing a temperature rise in the reactor. Similarly, the heat should be given to the desorption reaction without causing a temperature rise in the reactor. Therefore there is heat transfer limitation in these system s[49].

In order to improve the heat and mass transfer, suspending metal chloride in a solvent (gas-liquid-solid) is one possibility, but a better solution is to dissolve metal chlorides in a solvent and perform the reaction in gas-liquid phase. Therefore in this study, DES have been chosen as a solvent for $CaCl_2$ to increase the heat and mass transfer in $CaCl_2$-NH_3 reactions.

1.5. Properties of Chemicals Used in this study

The most important properties of DES components for their use in heat pump applications are their low cost and low vapor pressure. In this study, for the DES synthesis, it was proposed to use the chemicals like urea, choline chloride, and zinc chloride. Besides these, the most important properties that cause to be used in their effect on heat transfer coefficients and solubility properties. It was proposed that $CaCl_2$ is soluble in the synthesized DES and also it is proposed that the reaction in the liquid phase will increase heat and mass transfer. One of the disadvantages of the DES in chemical heat pump application is that, they are not thermally stable, and their viscosities are higher than most of the common solvents.

Urea which is also known as diaminomethane, has IUPAC name as CH_4N_2O. It is easily available and cheap. It is biocompatible and environmentally safe. The nitrogen in urea also makes it a good option for livestock feeds.

In literature, one of the most studied DES is choline chloride ($C_5H_{14}ClNO$) - urea which is also known as reline. The low cost and availability of both urea and choline chloride makes it the best candidate for industrial applications [60]. Choline chloride is also named as 2-hydrocyethly-trimethylammonium chloride. It is the most widely used component in DES studies as a hydrogen bond acceptor. The term 'deep eutectic solvent' first mentioned in a solvent made of choline chloride. Choline chloride widely used in the food industry as a chicken feed and its production rate is very high. It is an economic, nontoxic and biodegradable material. Zinc chloride is an ionic salt that is essential for the synthesis of cholesterol, protein, and fats. Zinc plays an important role in the proper functioning of the immune system. Zinc is required for the enzyme activities necessary for cell division, cell growth, and wound healing as well as the release of vitamin A from the liver. It plays a role in the acuity of the senses of smell and taste and is required to maintain prostate reproductive health and insulin function. Zinc is also involved in the metabolism of carbohydrates. Its IUPAC name is dichlorozinc.

CHAPTER 2

EXPERIMENTAL

The experimental part of this study consists of three parts. In the first part, the syntheses of DES were carried out. Two different types of DES which are zinc chloride ($ZnCl_2$) –urea DES and choline chloride (ChCl)-urea DES were synthesized at various molar compositions. In the synthesis of DES, two different commercial DES, which are zinc chloride ($ZnCl_2$) –urea DES and choline chloride (ChCl)-urea DES were selected. Their different molar compositions were studied. In addition to these, these two DES were mixed in different proportions in order to tune their properties. In the second part of the experiment, calcium chloride ($CaCl_2$) solubility measurements in different DES were conducted. By knowing the maximum soluble $CaCl_2$ amount, DES-$CaCl_2$ solutions and suspensions were prepared. In the third part of the experiment ammonia sorption experiments were conducted in order to see the ammonia reaction capacity of $CaCl_2$, $ZnCl_2$, urea, different DES's suspensions, and solutions.

2.1. Chemicals

Deep eutectic solvents were prepared by using zinc chloride (98%) (Sigma Aldrich, St. Louis, United States) (CAS Number: 7646-85-7), urea (%99) (Merck, New Jersey, United States) (CAS Number : 57-13-6) and choline chloride (98%) (Sigma Aldrich, St. Louis, United States)(CAS Number :67-48-1). The synthesis of DES were prepared under nitrogen atmosphere, where the Nitrogen Gas (99.9%) is purchased from Linde Gas. Solubility tests were done by using calcium chloride ($CaCl_2$) (%98) (Merck, New Jersey, United States) (CAS Number 7440-70-2). In addition, ammonia reaction experiments were carried out by using ammonia (%99.8) which was supplied from Seral Gas (CAS Number: 7664-41-7),

2.2. Synthesis of Deep Eutectic Solvents
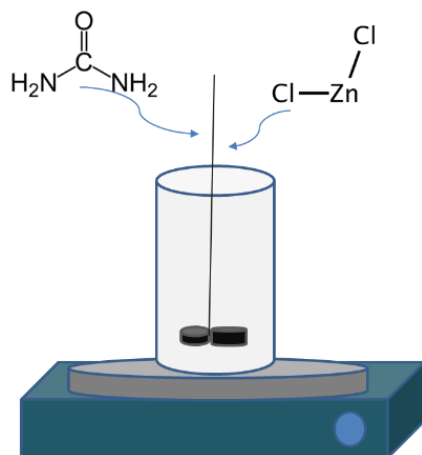
Figure 2.1. A scheme for the preparation of $ZnCl_2$-urea DES and the structures of urea and $ZnCl_2$.

$ZnCl_2$-urea DES samples were prepared by the method given in the literature [56]. Initially, $ZnCl_2$ and urea were dried in an oven at 90°C overnight in order to remove the moisture. After drying, $ZnCl_2$ and urea were mixed in different molar proportions and heated in an oil bath at 80 °C in glove bag under nitrogen atmosphere until the transparent homogeneous liquid was obtained (Figure 2.1). Glove bag is purchased from Glas-Col. Co., United States, and is made of 0.06 mm thick polyethylene, with integral gloves (Figure 2.2). The glove bag is filled with nitrogen gas in order to create an inert atmosphere with zero humidity for the synthesis of pure deep eutectic solvents.

Figure 2.2. A photograph of the glove bag used in this study.

Below the $ZnCl_2$:urea molar ratio of 2.0:10, the formation of a transparent liquid was not observed in the literature. Therefore, samples with $ZnCl_2$:urea molar ratios in the range of 2:10 to 4:10 were prepared (Table 2.1). The stabilities of the prepared DES samples were tested by storing the samples in isolated vials under atmospheric conditions until cloudiness was observed. In addition to $ZnCl_2$-urea, mixtures of calcium chloride- urea were also prepared at different molar ratios at 80°C. However, these experiments were not successful due to the lack of transparency of liquid samples and phase separations.

Table 2.1. *$ZnCl_2$-urea molar ratios of the synthesized DES*

$ZnCl_2$: urea (mol : mol)
2.0 : 10
2.5 : 10
3.0 : 10
3.5 : 10
4.0 : 10

One of the most commonly used DES is ChCl-urea which is also known as reline. Reline samples were prepared by following the same procedure that was used for $ZnCl_2$-urea samples by using three different molar ratios of choline chloride to urea. Reline formation was verified by the formation of a transparent homogenous liquid phase. The molar ratios of the prepared homogenous and transparent reline samples are given in table 2.2.

Table 2.2. *ChCl-urea molar ratios of the synthesized DES*

ChCl : urea (mol : mol)
1.0 : 2.0
1.5 : 2.0
1.0 : 1.0

The mixture of deep eutectic solvents of ChCl-urea (reline) and $ZnCl_2$-urea were prepared by using three different ratios at 80°C to explore the tunability of the solvent properties. From literature, it is known that $ChCl-ZnCl_2$, ChCl-urea and ZnCl-urea represent Type I, Type III and Type IV DES structures respectively. Therefore, it was considered that the mixture of these two types of DES (ChCl-urea and ZnCl-urea) might form a different type of DES having stability or longer lifetime. The molar ratios of the prepared homogenous and transparent mixture of reline and $ZnCl_2$-urea DES are given in table 2.3.

Table 2.3. *ChCl-urea : ZnCl$_2$-urea mixture molar ratios*

ChCl : urea (mol)	ZnCl$_2$: urea (mol)
1	0.5
1	1
0.5	1

2.3. Solubility measurements of $CaCl_2$ in $ZnCl_2$-urea DES

The solubility of $CaCl_2$ in $ZnCl_2$-urea DES at room temperature was tested by adding small amounts of $CaCl_2$ into DES sample and observing the formation of a homogenous transparent solution. First, 0.1 g calcium chloride was added to DES. After mixing and observing solubility $CaCl_2$ addition was continued. $CaCl_2$ was added in small incremental amounts (0.1 g), while the mixture was continuously stirred. The addition of $CaCl_2$ was continued until the cloudiness which indicates the saturation of DES sample with $CaCl_2$ was observed. The oversaturated mixture was then centrifuged for half an hour to precipitate the undissolved $CaCl_2$ and the homogenous saturated $CaCl_2$-DES solution was obtained. The concentration of $CaCl_2$ in the solution was detected with an inductively coupled plasma (ICP) (Perkin Elmer DRC II, USA).

2.4. Solubility Measurements of $CaCl_2$ in ChCl-urea DES

The solubility and $CaCl_2$ in ChCl-Urea DES was also tested by using the same procedure that was mentioned above. Even in the first attempt, it was found that $CaCl_2$ was not soluble in reline.

2.5. Ammonia Sorption Experiments

The ammonia sorption experiments were conducted in a static sorption system which consists of a visible high-pressure vessel with sapphire windows, pressure transducer, temperature transducer, and a water circulation heater. The ammonia gas cylinder is connected to the system and pressure is regulated by two stage gas regulator. Figure 2.3 shows the experimental setup for ammonia sorption experiments.
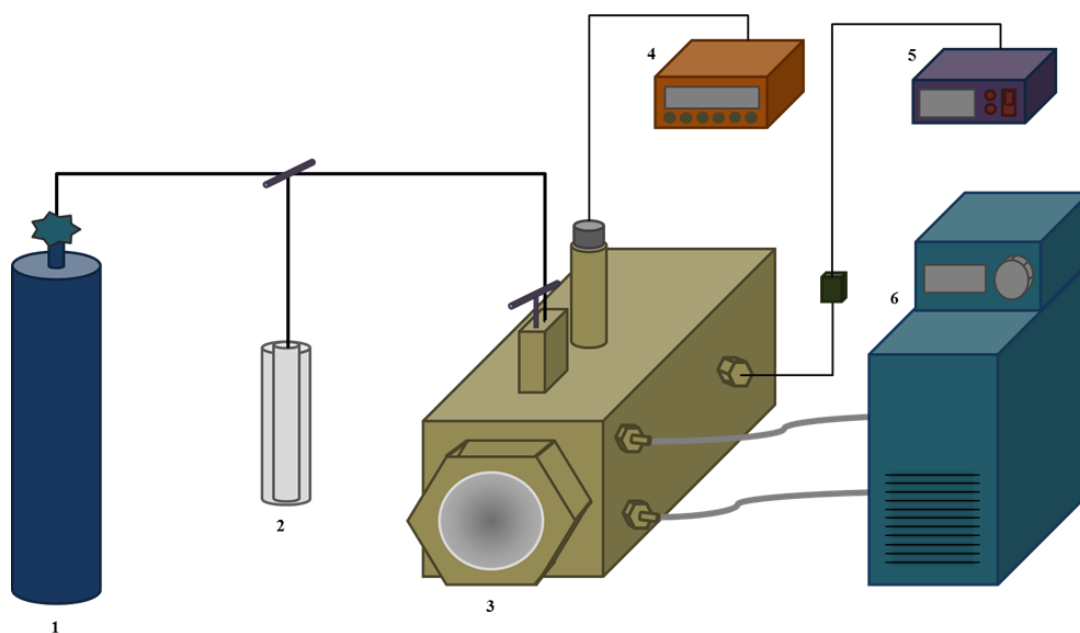
Figure 2.3. Experimental setup for ammonia reaction experiments; 1: ammonia tank, 2: gas washing bottle connected to the line with a three-way stop cock, 3: visible vessel, 4: pressure transducer, 5: temperature transducer, 6: water circulation heater.

The vessel was jacketed in order to control the temperature and connected into a thermostatic water circulator (Polyscience, 9112) which controls the temperature within a range of ± 0.01 °C. The interior volume of the vessel was 30.6 ± 0.05 ml. The vessel was coupled with a thermocouple (Omega Engineering KMQXL-IM150U-150, ± 0.5 °C) and pressure transducer (Omega Engineering PX419, ± %0.05). The vessel was connected to an ammonia tank thorough a three-way valve and stainless-steel tubing, connecting the cell to the ammonia tank and a gas washing bottle, which is used to trap the ammonia during the evacuation of the contents of the vessel. The experimental apparatus is located in a hood for safety.

The weighted amount of sorbent sample in a Pyrex cuvette was placed in the vessel. The vessel was closed, the temperature and pressure transducers were connected, and the water circulator was connected to the cell. The temperature was set to 25 °C to conduct the isothermal sorption experiments. The air within the system is purged through the three-way valve. Next, ammonia was loaded into the vessel slowly until the vessel pressure reaches 2 bar. The time course of gage pressure was recorded.

When the pressure decrease ceased to equilibrium value, the system was pressurized again. Overall, five cycles were carried out following the same procedure for different sorbent samples, which are $ZnCl_2$, urea, $CaCl_2$, DES, DES-$CaCl_2$ suspension, Reline DES, Reline-$CaCl_2$ suspension and Reline-$ZnCl_2$-urea mixture. The amount of samples used in the ammonia sorption experiments is given in Table 2.4.

Table 2.4: *Amount of samples used in ammonia sorption experiments*

Samples		m (g)
$CaCl_2$		2.17
$ZnCl_2$		2.83
Urea		3.83
$ZnCl_2$-Urea DES(3:10)		5.47
	$ZnCl_2$	2.22
	Urea	3.26
$ZnCl_2$-Urea DES+$CaCl_2$ Suspension		7.43
	$CaCl_2$	2.10
	$ZnCl_2$-Urea DES	5.33
	$ZnCl_2$	2.16
	Urea	3.17
ChCl-Urea DES (1:2)		5.40
	ChCl	3.78
	Urea	1.62
ChCl-Urea DES -$CaCl_2$ Suspension		7.75
	ChCl-Urea DES	5.53
	ChCl	3.87
	Urea	1.66
	$CaCl_2$	2.21
ChCl-$ZnCl_2$-Urea		7.38
	ChCl	2.46
	$ZnCl_2$	1.24
	Urea	3.68

The experiments were ceased at the end of the fifth cycle. The amount of ammonia sorbed was calculated from the density of the ammonia (obtained from the NIST Chemistry Web-Book at 25°C and the recorded pressure) and the volume occupied by ammonia in the vessel. The gas volume was calculated by considering the total inner volume of the vessel, the volume of the sorbent calculated from the mass and the density of the sorbent and the volume of the pyrex cuvette. For the DES-$CaCl_2$ suspension, the volume was determined by assuming additive volumes of solid and liquid phases.

2.6. Analyses

Fourier transform infrared spectroscopy (FTIR), thermogravimetric analyses (TGA), differential scanning calorimetry (DSC) and inductively coupled plasma (ICP) and karl fischer titration were used for sample characterization.

2.6.1. Fourier-transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analyses of deep eutectic solvents and their precursors, and their samples sorbed with ammonia as well as calcium chloride were performed by using a Perkin Elmer Spectrum One FTIR equipment with a wavenumber range of 500-4000 cm^{-1} and a resolution of 4 cm^{-1}.

2.6.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analyses (TGA) were performed by using Shimadzu TA-60 WS under nitrogen atmosphere at a temperature range of 25°C and 500°C, with a heating rate of 10°C/minute.

2.6.3. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) analyses were performed with Perkin Elmer Diamond Differential Calorimetry 8000 system under nitrogen atmosphere. The

applied temperature range was between -65°C and 65°C with a heating rate of 3°C/min.

2.6.4. Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) analyses were performed with Perkin Elmer DRC II model ICP-MS equipment which is located in Central Laboratory at Middle East Technical University. Before the analysis, the analyzed samples were dissolved in pure water. To increase the solubility one droplet of hydrofluoric acid was added to the pure water.

2.6.5. Karl Fischer Titration

Karl Fischer titration analysis were performed with Metrohm 701 KF Titrino model Karl Fischer Titration equipment which was done by Metrohm İstanbul office.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. DES Synthesis

The formation of deep eutectic solvents of $ZnCl_2$-urea and ChCl-urea mixtures were ensured by the formation of transparent homogenous liquid and transparency is sustained after cooling to room temperature. The DES samples were characterized by FTIR spectrometry. In addition to these, the stability of DES samples were tested. There is a lifetime of $ZnCl_2$-urea DES, but reline does not change in time so there is no lifetime of it.

3.1.1. $ZnCl_2$ based DES

The molecular structure of urea and $ZnCl_2$ is given in Figures 3.1 and 3.2. In the formation of DES and FTIR spectrometry, these structures play a crucial role.
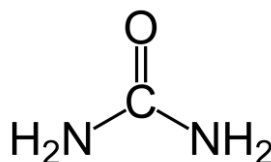
Figure 3.1. Chemical structure of urea[57]
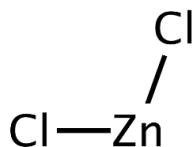
Figure 3.2. Chemical structure of $ZnCl_2$[58]

$ZnCl_2$ is a hygroscopic chemical that can pose a water contamination problem. In order to avoid the water impurity, the ingredients of $ZnCl_2$ -urea DES, the components were dried in the oven for 1 day at 90°C. After drying they were mixed. Before mixing

at 80°C, the mixture of $ZnCl_2$ and urea looks like a white powder crystal. The photograph of the mixture before heating is given in Figure 3.3a.

a)   b)
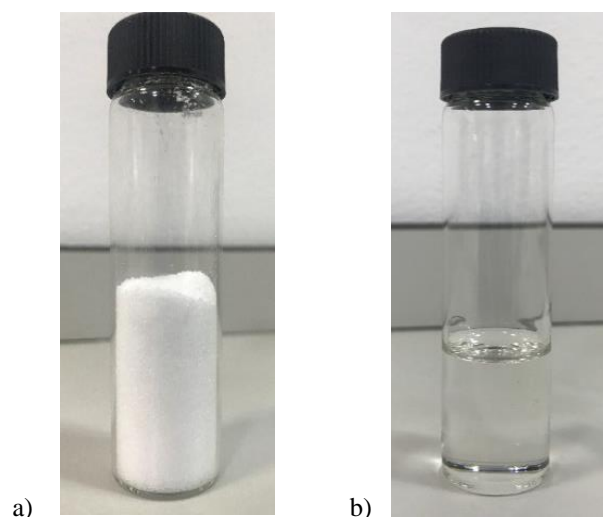
Figure 3.3. The mixture of $ZnCl_2$ and urea a)before heating and formation of DES b) after heating and formation of DES

After the formation of DES at 80°C, the mixture changed into homogeneous transparent high viscosity solvent which is sustained at room temperature. The photograph of DES is given in Figure 3.3b.

3.1.1.1. Stability analysis

The stabilities of the deep eutectic solvents were determined as the time between the formation of the homogenous transparent liquid and the formation of the cloud, loss of transparency or precipitation of solid phase. The sample photograph of the formation of cloudy mixture with eye inspection in 3:10 molar ratio $ZnCl_2$-urea DES after 30 days is shown in Figure 3.4.

Figure 3.4. ZnCl$_2$ -urea DES at its lifetime

In Table 3.1., the stability of the deep eutectic solvents under ambient conditions are given in terms of the numbers of days. The results are similar and in good agreement with literature except the 2.5:10 molar ratio, for which we observed a stable solution for 5 days whereas their report states a longer period [22]. The stability tests show that the most stable deep eutectic solvent is the one with the zinc chloride-urea ratio of 3.0:10, which is also inconsistent with the study reported by Lian et al. [22] Therefore, 3:10 molar ratio of ZnCl$_2$-urea was selected and applied in the rest of the studies.

Table 3.1. *Lifetime of ZnCl$_2$-urea DES formed at* ambient conditions.

Molar Ratio (ZnCl$_2$:urea)	Lifetime (days)
2.0 : 10	10
2.5 : 10	5
3 : 10	30
3.5 : 10	14
4 : 10	2

3.1.1.2. FTIR analysis of ZnCl$_2$-urea DES

The formation of the DES was verified with FTIR analyses which gave important information about the intermolecular interactions between the ZnCl$_2$ and urea. The FTIR spectra of urea, ZnCl$_2$, and ZnCl$_2$-urea DES (3:10 molar ratio) are given in Figure 3.5.
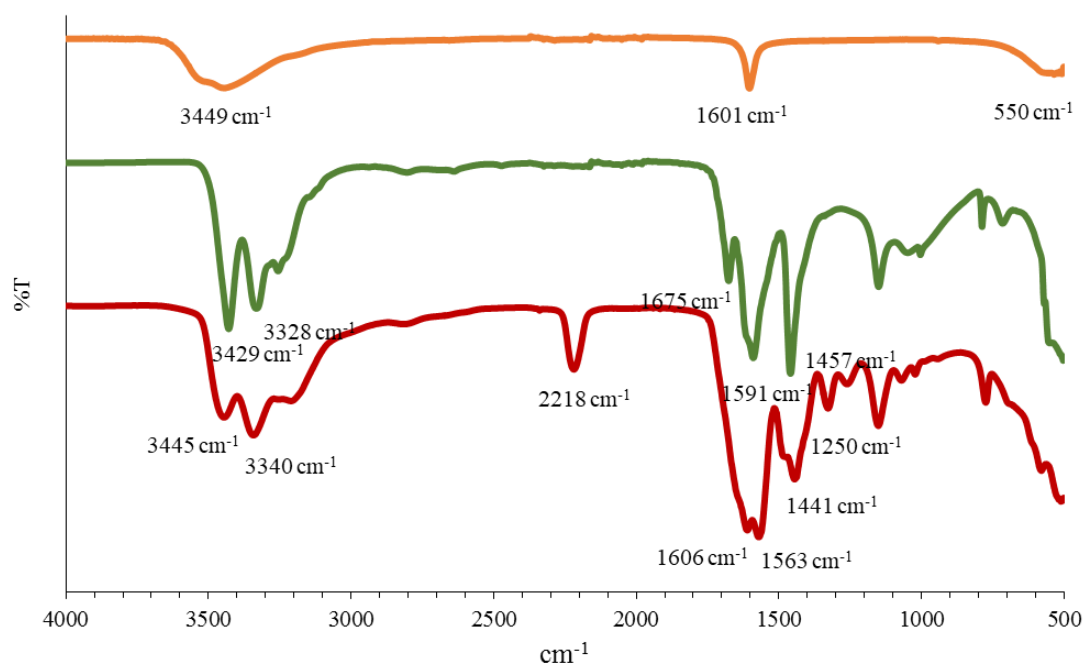
Figure 3.5. *FTIR spectra of ZnCl$_2$, urea, ZnCl$_2$ -urea DES (Orange line: ZnCl$_2$, Green line: urea, Red line: ZnCl$_2$ -urea DES)*

ZnCl$_2$ is a transition metal salt with a triatomic structure, which shows s-p hybridization that may exhibit four modes of vibrations in the FTIR spectrum [59] and the metal halide Zn-Cl peak appears in the range of 750-100 cm^{-1} in the FTIR spectrum [60]. The peak at 550 cm^{-1} is due to the Zn-Cl stretching. The peak at 1601 cm^{-1} and wide absorption bands around 3450 cm^{-1} are ascribed to the H-O-H bending and O-H stretching modes that are associated with the adsorbed water due to the hygroscopic nature of ZnCl$_2$.

The FTIR spectrum for pure urea is also given in Figure 3.1, where the carbonyl C=O stretching was observed at 1675 cm^{-1} [61]. The wide peaks observed in the

wavenumber range of 3300-3500 cm^{-1} are assigned to the stretching modes of N-H. Due to the formation of DES, the C=O stretching band shifted to 1606 cm^{-1}. The stretching vibration frequency shifting to lower wavenumber (red shift) indicates the interaction of carbonyl group of urea with Zn^{+2}. The metal-urea complexes preferably form through the metal and the carbonyl oxygen rather than the metal and nitrogen of the amino groups of the urea, which would lead to a shift to higher wavenumber [61] [22][62].

New peaks observed at 2218 cm^{-1} and 1250 cm^{-1} in DES spectrum are attributed to the asymmetric and symmetric stretching modes of Zn^{+}–O–C=N and Zn^{+}–O=C–N resonant structures, as a result of the complex formation between the urea and ZnCl$_2$ [22]. As a result of the intermolecular interactions between urea and ZnCl$_2$, the N-H stretching modes are also shifted to 3445 cm^{-1} and 3340 cm^{-1}. Similarly, the peaks in the pure urea spectrum at the wavenumbers of 1591 cm^{-1} and 1457 cm^{-1}, which corresponds to the bending mode of NH$_2$ decreases to 1563 cm^{-1} and 1441 cm^{-1} in the spectrum of DES possibly due to the hydrogen bonding between the protons of NH$_2$ and the chlorine anions. The intermolecular interaction between oxygen of the urea carbonyl and Zn cation leading to the red shift in the FTIR analysis is the reason behind the DES formation of ZnCl$_2$ and urea[62]. This strong interaction weakens the Coulombic forces between the zinc cation and the chloride anion, and causes the formation of the coordination complexes between the Zn cation and urea, increasing the size of the Zn cation which results in decreasing the melting point of the mixture[22].

3.1.2. Reline DES

The molecular structure of urea and choline chloride is given in Figure 3.1 and Figure 3.6 respectively.
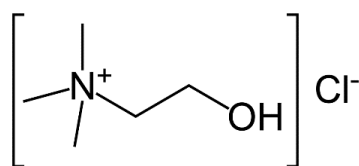
Figure 3.6.Chemical structure of choline chloride (ChCl)[63]

Prior to the DES synthesis experiments, both choline chloride and urea were dried in an oven overnight at 90°. Before heating, the mixture of ChCl and urea looks like white powder crystals with a distinct odor. The molar ratio of choline chloride to urea was chosen as 1:2 because it is the most commonly used molar ratio of the DES. In addition to this, Li et al studied the solubility of CO_2 in DES systems formed with choline chloride and urea of three molar ratios (1:1.5, 1:2, 1:2.5) at different temperatures and reported that 1:2 molar ratio is the best composition for maximum solubility of CO_2 [64] [63]. 1:2 molar ratio of choline chloride to urea is the most widely used ratio therefore in this study this ratio was chosen.

The optical stability analysis of reline was also performed. The stability tests were continued for 30 days and experiments were ceased because no cloud, precipitation or opacity was observed. More than 6 months was waited and there was no change in the homogeneity and transparency in the reline. In literature, there is no information about the lifetime and stability of reline under ambient conditions.

3.1.2.1. FTIR Analysis of Reline

In order to define the microstructure of reline, FTIR analysis was carried out. The FTIR spectra of reline DES, urea and choline chloride is given in Figure 3.7.
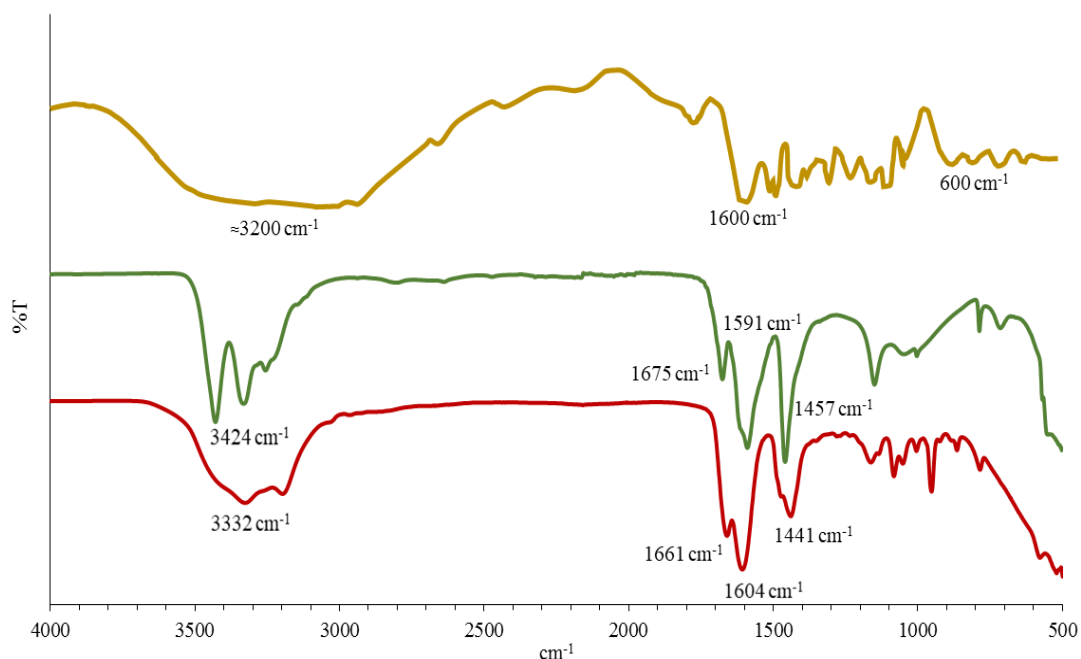
Figure 3.7. FTIR spectra of ChCl-urea DES (*Yellow line: ChCl, Green line: urea, Red line: ChCl-urea DES)*

The absorption band at 3332 cm^{-1} is wider than the band in urea at 3427 cm^{-1} and in ChCl at 3200 cm^{-1}. This is because of the formation of more hydrogen bonds between urea and choline chloride. [65]. These bonds can be in the form of N-H…N-H, N-H…O-H, H-O…O-H and O-H…N-H.). The asymmetric stretching of NH_2 at 1552 cm^{-1} and 1675 cm^{-1} shifted to 1604 cm^{-1} and 1661 cm^{-1} in reline DES. The interaction of CH_3 and ChCl lead to the peak at 1441 cm^{-1} in reline DES. The presence of the ammonium functional group in choline chloride is observed in reline in the region between 3000 and 3500 cm^{-1}[66]. The peaks at 3316 cm^{-1} and 3194 cm-1 are assigned to asymmetric and symmetric stretching of NH_2 [67]. In the spectra at the wavenumber 1665 cm^{-1}, there is C=O stretching vibration[68]. The peaks at 1601 cm^{-1} and 1652 cm^{-1} are the vibrations of $C=ONH_2$[12].

3.1.3. $ZnCl_2$ -urea & reline DES

$ZnCl_2$-urea and reline mixtures were prepared by mixing the samples of $ZnCl_2$-urea (3.5:10 mol/mol) and reline (1:2 mol/mol) in certain ratios. The aim behind this study

is to prepare a solvent with a longer lifetime and higher $CaCl_2$ solubility. Unfortunately, their mixtures are not stable than their pure counterparts and it is clearly seen that mixing different deep eutectic solutions causes loss of stability to a large extent. In table 3.2., the stability of reline and $ZnCl_2$-urea DES mixtures are given. As it can be seen from the table, the most stable mixture is in a molar ratio of 1 reline : 0.5 ZnCl-urea DES

Table 3.2. *The lifetimes of ChCl:urea and ZnCl$_2$:urea mixtures*

ChCl : urea (mol)	$ZnCl_2$: urea (mol)	Lifetime
0.5	1	< 1 hour
1	1	< 1 hour
1	0.5	1 hour

In Figure 3.8, the photographs of the changes of the mixture of $ZnCl_2$-urea and ChCl-urea DES in 1:0.5 ratio is given. The changes occured less than one hour.

Figure 3.8. Changes of the mixture of $ZnCl_2$-Urea and reline mixture in 1:1 molar ratio.

As the most stable mixture of solvents is in 1:0.5 ratio of $ZnCl_2$-urea to reline, the sample of this solvent mixture was analyzed in FTIR immediately after preparation.

The FTIR spectrum of 1:0.5 ratio of $ZnCl_2$-urea to reline mixture is given in Figure 3.9.
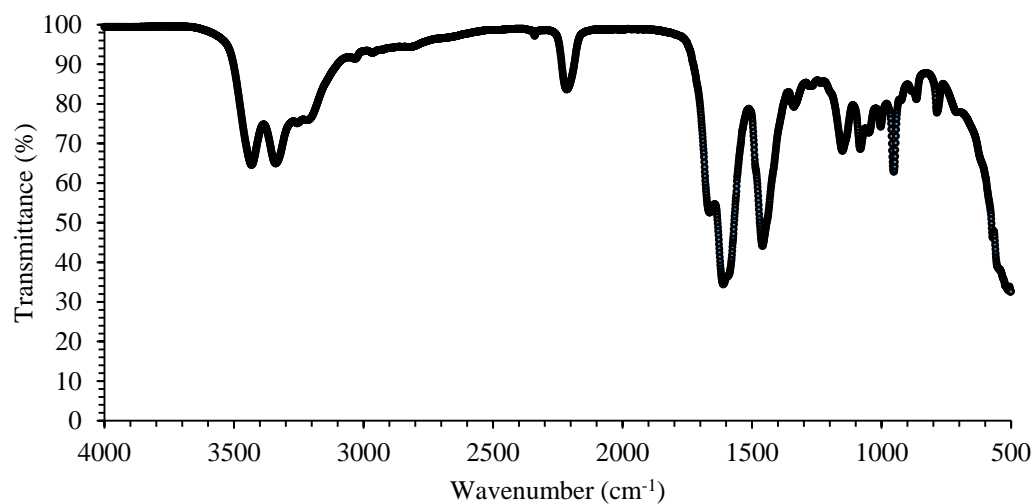
Figure 3.9. The mixture of reline DES and $ZnCl_2$ -urea DES

The FTIR spectra of a mixture of ChCl-urea and $ZnCl_2$-urea DES is the combination of each component which indicates the formation of physical mixture. The peaks at 3333 cm^{-1} and 3431 cm^{-1} are ascribed to the stretching modes of N-H. As it was observed in $ZnCl_2$-urea DES the asymmetric and symmetric stretching modes of Zn^+–O–C=N and Zn^+–O=C–N resonant structures appear at 2210 cm^{-1} and 1606 cm^{-1}.

3.2. Solubility of $CaCl_2$ in DES

Calcium chloride solubility in $ZnCl_2$-urea at room temperature was determined in three DES samples having different $ZnCl_2$-urea molar ratios. After mixing the DES sample with $CaCl_2$, the mixture was centrifuged a centrifuge to accumulate the insoluble fraction of solid $CaCl_2$. Each samples were centrifuged for 30 minutes. At the end of the centrifugation, two different phases were observed in the sample. The top portion was suggested as the soluble $CaCl_2$ containing DES and the bottom fraction was considered as were solid $CaCl_2$ in DES. Samples from the top layer were analyzed in the ICP. The analyzed part of the mixture have been shown schematically in Figure 3.10 as part A and part B is the nontransparent suspension mixture of $CaCl_2$ and DES.

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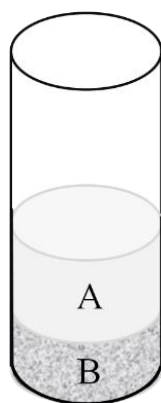
Figure 3.10. A schematic shown of the DES and CaCl$_2$ mixture after the centrifuge. (Part A is the transparent part where CaCl$_2$ is soluble in DES and part B is the nontransparent suspension part)

In order to increase the precision, two sets of experiments were performed in three different molar ratios. In total 6 different samples were tested. Before the analysis, the samples were diluted with pure water which is a requirement of the ICP equipment.

The calcium contents of the samples are determined and given in Appendix A in Table A.1. With the known mass of the CaCl$_2$ in the solutions, CaCl$_2$ weight content of solvents were calculated and tabulated in Table 3.3. The highest solubility of CaCl$_2$ was observed in the DES with the ZnCl$_2$-urea molar ratio of 2.5:10, which was 5.3 wt.%. The results show that the solubility of CaCl$_2$ decreases with increasing ZnCl$_2$:urea molar ratio.

Table 3.3. *ICP Results in terms of CaCl$_2$*

ZnCl$_2$-urea molar ratio	1st Sample wt.% CaCl$_2$ (± 0.1)	2nd Sample wt.% CaCl$_2$ (± 0.1)	Average wt.% CaCl$_2$ (± 0.1)
2.5:10	5.4	5.2	5.3
3.0 :10	4.7	4.7	4.7
3.5 : 10	3.6	3.8	3.7

In reline samples, the solubility of $CaCl_2$ could not be detected by using the applied experimental method. Even a tiny amount of $CaCl_2$ was not dissolved in reline sample at room temperature, showing that $CaCl_2$ is insoluble in reline DES.

3.3. Karl Fischer Titration Results

As the chemicals involved in deep eutectic solvent is hydrophilic, water content is important. The water content of the DES samples were determined by Karl Fischer Titration. Water content of $ZnCl_2$-urea DES and $ZnCl_2$-urea-$CaCl_2$ suspension are given in Table 3.4.

Table 3.4. Karl Fischer titration results for $ZnCl_2$-urea DES and $ZnCl_2$-urea-$CaCl_2$ suspension

Sample	% Water Content
Zinc chloride + urea	0.46 ± 0.015
Zinc chloride + urea + calcium chloride	1.07 ± 0.015

The water content in the suspension is higher than pure deep eutectic solvent which can be explained by the hygroscopic nature of $CaCl_2$. The water will restrain the ammonia reaction so after these results, a glove bag was started to be used during the synthesis. Samples were stored in sealed vials in order to prevent the water absorption into the samples.

Similarly, synthesis of reline samples were also carried out in a glove bag. Du et al. have reported the water content of reline in 1.0:2.0 molar ratio (ChCl:urea) which was waited in atmospheric conditions. They have used Karl Fischer Titration and they reported the water content of reline as 0.23 ± 0.01 % . [32]. These results indicate that reline is not hygroscopic as $ZnCl_2$-urea DES samples.

3.4. Sorption of ammonia with DES/CaCl$_2$

Ammonia sorption experiments were conducted by loading the known mass of the DES sample into the cell by using a static method. The system kept at constant temperature at 25°C. In order to calculate the initial and final concentrations of ammonia gas in the cell, it was assumed that the vapor phase consists only of ammonia since the DES has a low vapor pressure and can be neglected. In addition to this, the change in the volume of the sample was neglected. The amount of ammonia sorbed was calculated by using the density of the ammonia given by NIST for 25°C and the recorded pressure of ammonia in the vessel. Based on these assumptions, the amount of sorbed ammonia was calculated using the Equation 5.

$$\Delta n_{NH_3} = \frac{\Delta \rho \times V}{M_{w_{NH_3}}} \hspace{3cm} \text{Equation 5}$$

Where n_{Nh_3} is the number of mols of ammonia sorbed, $\Delta \rho$ is the change of ammonia density due to the pressure changes, V is the volume covered by ammonia in the cell and $M_{w_{Nh_3}}$ is molecular weight of ammonia.

Ammonia sorption into ZnCl$_2$-urea (3.5:10 mol/mol) and ChCl-urea (1:2 mol/mol) DES samples and their CaCl$_2$ suspensions were examined by applying five successive sorption cycles. The first ammonia sorption cycle for ZnCl$_2$-urea DES-CaCl$_2$ suspension and pure CaCl$_2$ samples are given in Figure 3.11. In the first cycle, ZnCl$_2$-urea (3.0:10 mol/mol) DES-CaCl$_2$ suspension exhibited slightly higher sorption rate than pure CaCl$_2$, and at the end, a higher ammonia amount of sorption was observed in ZnCl$_2$-urea (3.0:10 mol/mol) DES-CaCl$_2$ suspension. At the end of the first cycle, the ZnCl$_2$-urea (3.0:10 mol/mol) DES-CaCl$_2$ suspension sorbed with 1.12 mmol ammonia per gram of CaCl$_2$ while pure CaCl$_2$ sorbed with 0.90 mmol ammonia per gram of CaCl$_2$. It corresponds to the sorption stoichiometry of 0.12 mol ammonia sorption per mol of CaCl$_2$ and 0.1 mol ammonia per mol of CaCl$_2$ in suspension and pure solid CaCl$_2$ respectively which are far away from saturation (2 moles of NH$_3$/mole CaCl$_2$).
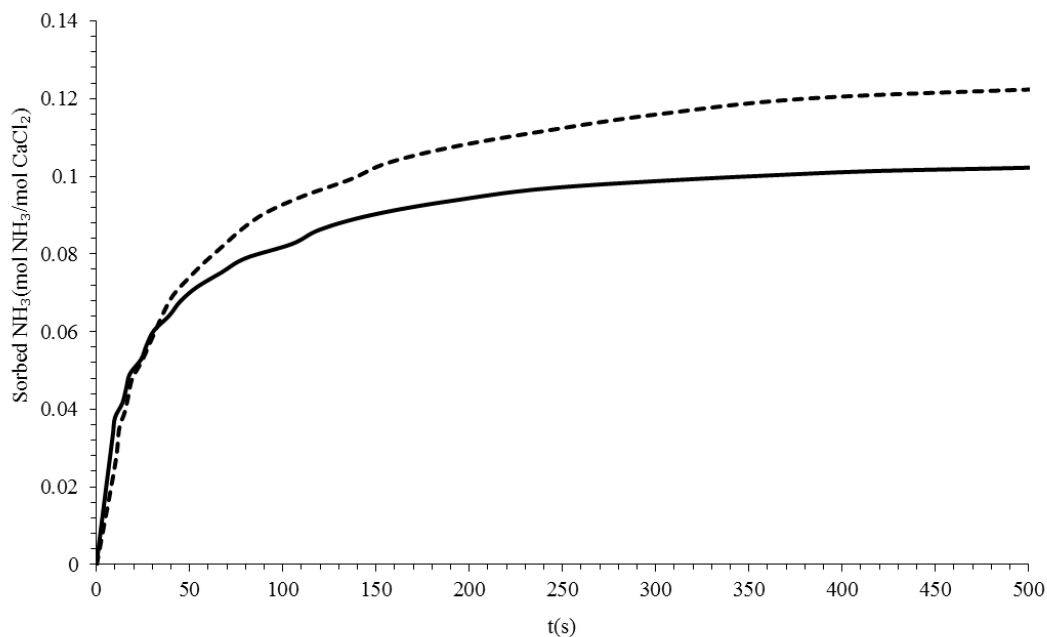
Figure 3.11. *First sorption cycle using pure CaCl$_2$ and ZnCl$_2$-urea DES-CaCl$_2$ suspension. (━━ CaCl$_2$ - - - DES+CaCl$_2$)*

After reaching the first cycle equilibrium, the cell was repressurized by introducing more NH$_3$ and the sorption data was recorded again as pressure versus time until the equilibrium was reached. The sorption data were collected between 2 and 0.1 bar pressure range at 25°C. Overall, five cycles were completed. The sorbed ammonia of all the cycles versus time plots for CaCl$_2$ and ZnCl$_2$-urea DES-CaCl$_2$ suspension are given in Figure 3.12. As it is shown in the figure, in all cycles, the ZnCl$_2$-urea DES-CaCl$_2$ suspension exhibited a higher ammonia sorption than CaCl$_2$. The total number of mols of sorbed ammonia per gram of CaCl$_2$ at the end of the fifth cycle determined for ZnCl$_2$-urea DES-CaCl$_2$ and CaCl$_2$ were 3.36 mmol and 2.76 mmol, respectively.
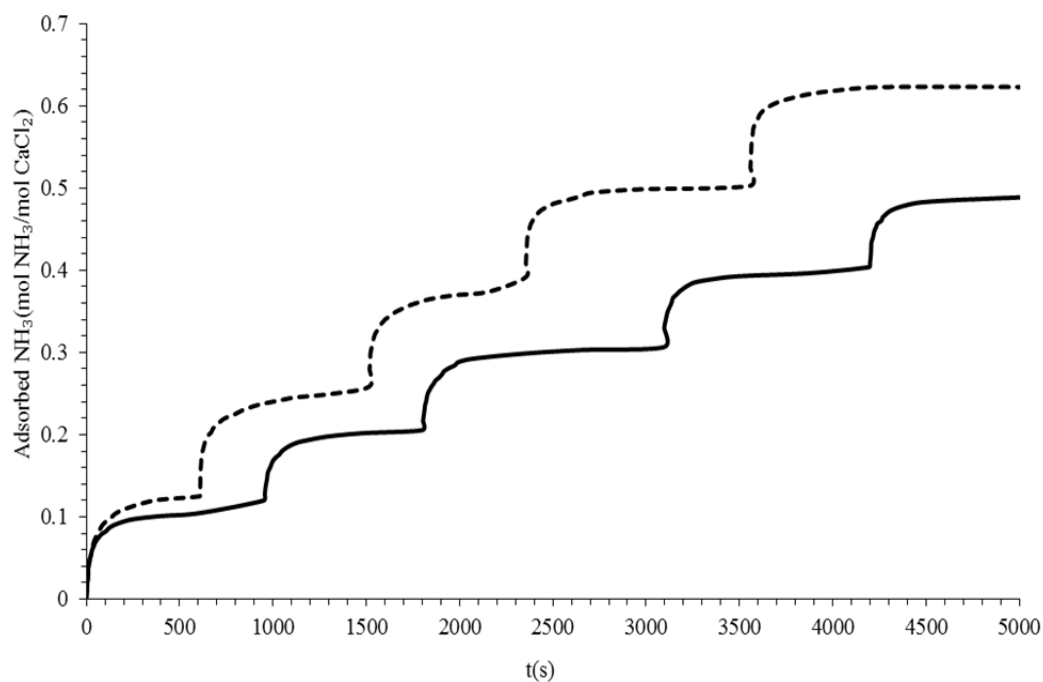
Figure 3.12. Sorbed ammonia per mol of $CaCl_2$ versus time graph for $CaCl_2$ and DES-$CaCl_2$ suspension (——$CaCl_2$ - - - DES+$CaCl_2$)

At the end of the experiments, a layer was observed at the top of the DES sample through the sapphire windows of the sorption cell. A picture of the layer formation is given in Figure 3.13. It was thought that, it is the $CaCl_2$-ammonia complex layer.
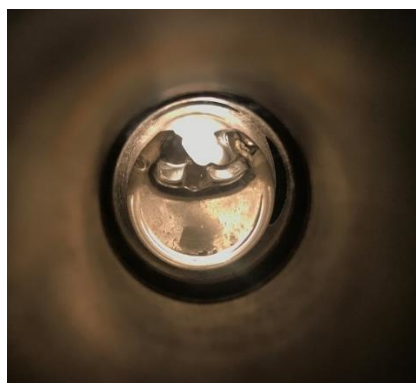
Figure 3.13. A picture of ammonia sorbed $ZnCl_2$-urea DES- $CaCl_2$ suspension

Unfortunately, it was impossible to evaluate its components in this system because when the cell opened to the atmosphere, the layer diminishes by desorption of

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ammonia. The FTIR spectra of the upper phase and lower phase is given in Appendix B in Figure Figure A.1.

It was found that the $ZnCl_2$-urea DES-$CaCl_2$ suspension absorbs a higher amount of ammonia than pure $CaCl_2$. This is possibly due to the sorption of ammonia by $ZnCl_2$, which was reported in the literature[69]. Similar to $CaCl_2$, ammonia sorption on $ZnCl_2$ takes place with different stoichiometry depending on temperature and pressure. The reversible zinc chloride – Ammonia sorption reaction is given in Rxn 3.1[70].

$$ZnCl_2(s) + 2NH_3(g) \leftrightarrow ZnCl_2 \cdot (NH_3)_2(s) \hspace{3cm} \text{Rxn 3. 1}$$
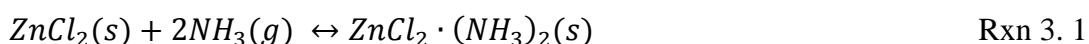
For which the thermodynamic functions at ΔH^0, ΔG^0 and $T\Delta S^0$ (at 25°C) are -170 kJ/mol, -111 kJ/mol and -59 kJ/mol respectively.

Therefore, during the experiments ammonia sorption into both $CaCl_2$ and $ZnCl_2$ may take place. This possibility was tested and verified by another set of sorption experiments. The ammonia sorption was studied over $ZnCl_2$-urea DES and the results were compared with those of pure $ZnCl_2$ that was used at the same amount as in the $ZnCl_2$ -urea DES sample. The results are shown in Fig 3.14.
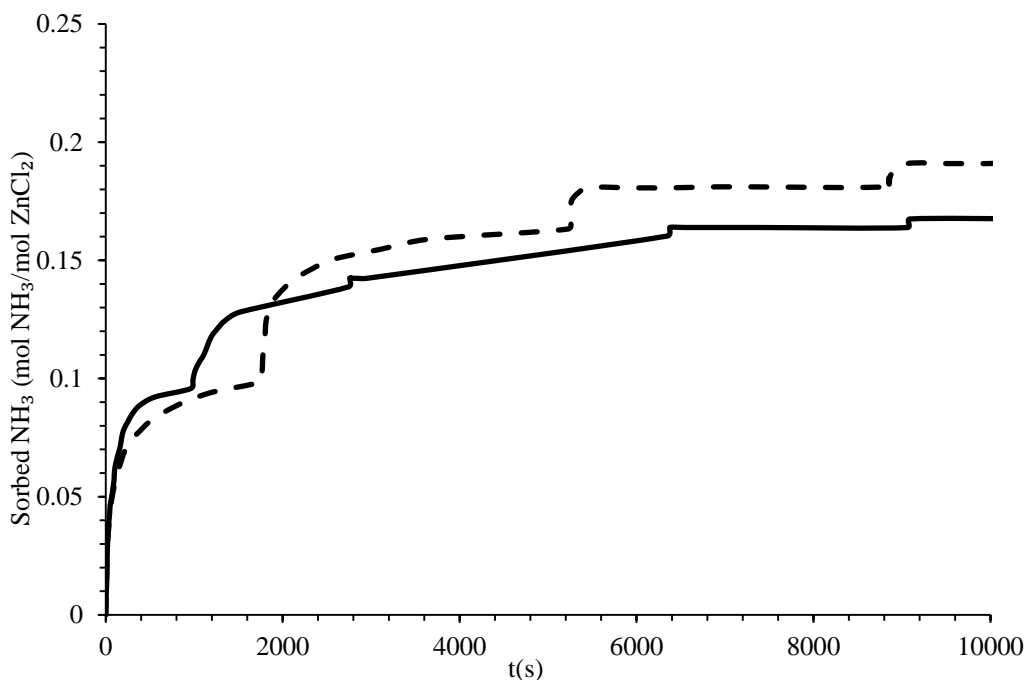
Figure 3.14. Ammonia sorption onto $ZnCl_2$ and $ZnCl_2$ -urea DES at 25°C and 2-0.1 bar. (--------- DES - - - $ZnCl_2$)

Figure 3.15 shows the mols of ammonia sorbed by $ZnCl_2$ and by $ZnCl_2$ -urea (3.0:10) DES, both as per mol of $ZnCl_2$. The amount of $ZnCl_2$ used in the sorption experiment using DES was the same with that used in the sorption experiment using pure $ZnCl_2$. It is clearly seen that the rate and the amount of ammonia sorption into the solid $ZnCl_2$ is almost the same with the rate observed in $ZnCl_2$-urea DES. These results show that the higher amount of ammonia sorbed by $CaCl_2$- $ZnCl_2$-urea DES suspension compared to pure $CaCl_2$ is due to the ammonia sorption by $ZnCl_2$ in DES. The control experiments were also performed by urea and as it is shown in Figure 3.15, the amount of ammonia sorption into urea is much smaller than $ZnCl_2$-urea DES and therefore, it is negligible. These results prove the advantage of using DES-$CaCl_2$ suspension for the ammonia sorption process and reveal the enhanced ammonia sorption of $ZnCl_2$ based deep eutectic solvents.

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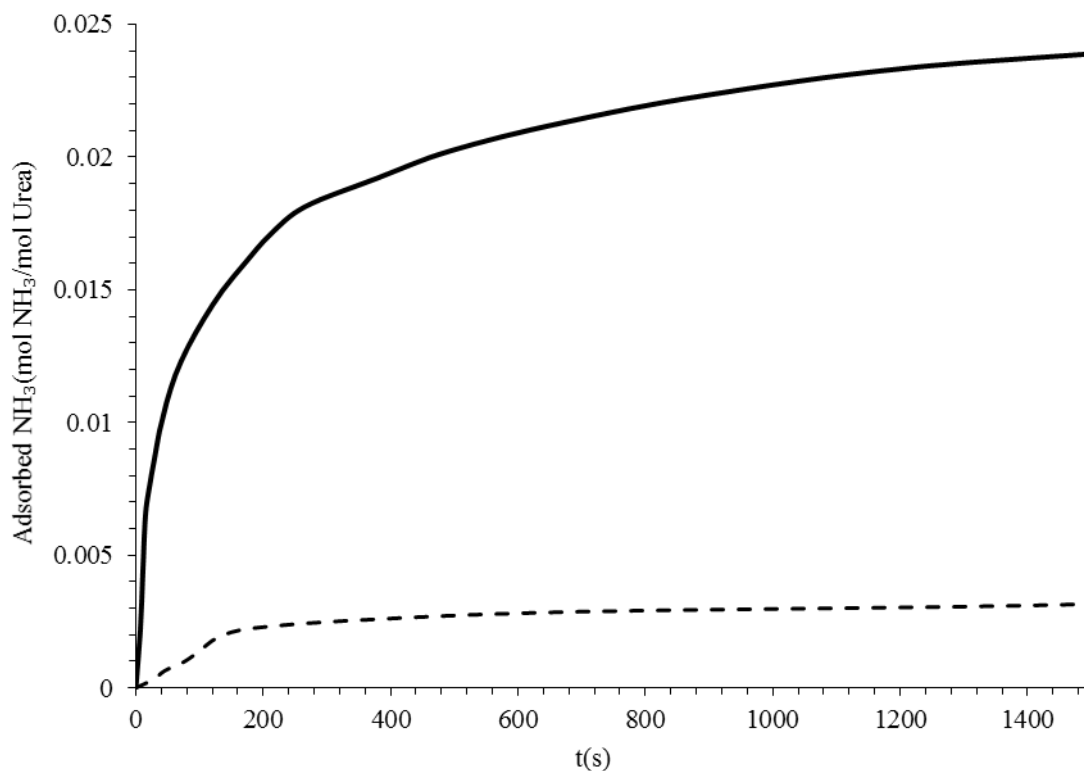
Figure 3.15. Ammonia sorption onto urea and $ZnCl_2$-Urea DES (⸻DES - - - - - Urea)

The ammonia sorption in $ZnCl_2$-urea DES seems advantageous and sorption is favored by both $CaCl_2$ in suspension and $ZnCl_2$ in the DES.

The type of DES in ammonia sorption was also tested and the ammonia sorption into $ZnCl_2$-urea DES was compared with ChCl-urea DES. As it is shown in Figure 3.16, the ammonia sorption amount is higher into 0.4 g $CaCl_2$/ g $ZnCl_2$-urea DES than the 0.4 g $CaCl_2$/g ChCl-urea DES where these two suspensions contain same amount of $CaCl_2$. In addition to these, the sorption into 0.4 g $CaCl_2$/g ChCl-urea DES takes place with a slower rate than 0.4 g $CaCl_2$/ g $ZnCl_2$-urea sample under the tested experimental conditions.
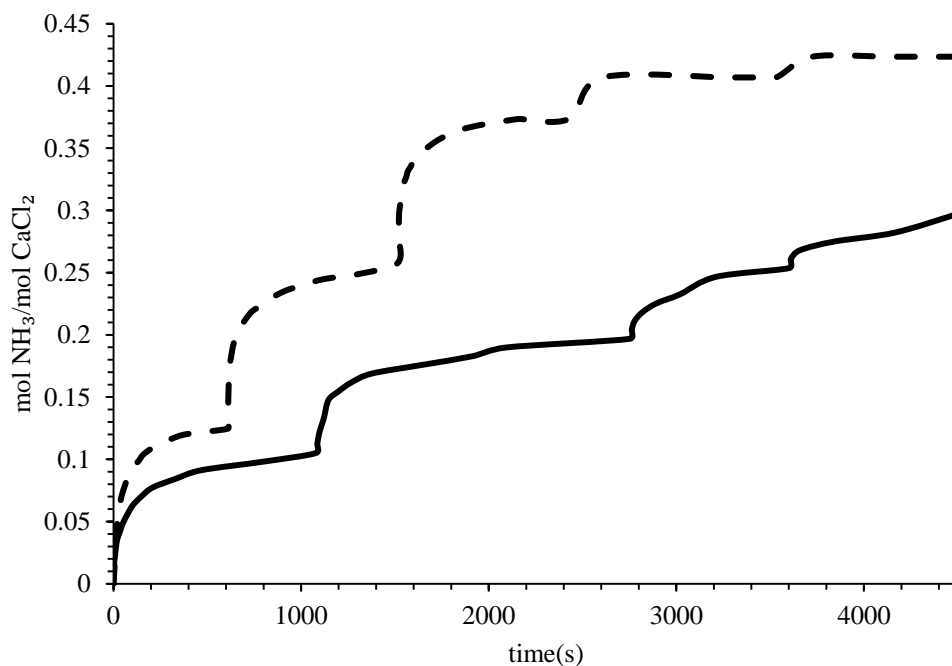
Figure 3.16. Sorbed ammonia per mol of $CaCl_2$ versus time graph of $CaCl_2$ suspensions with ZnCl-urea DES and reline DES (⸻ $ZnCl_2$ -Urea DES (3.0:10) + $CaCl_2$ (0.4 g $CaCl_2$ /g DES); - - - - : ChCl-Urea DES (1:2) + $CaCl_2$ (0.4 g $CaCl_2$ /g DES))

Although the ammonia sorption properties of $ZnCl_2$-urea DES is better than reline, it has an important stability problem as it was discussed previously. In addition, it has a higher viscosity than reline. Therefore, reline and $ZnCl_2$-urea mixtures were also tested for ammonia sorption and the results are shown in Figure 3.17.

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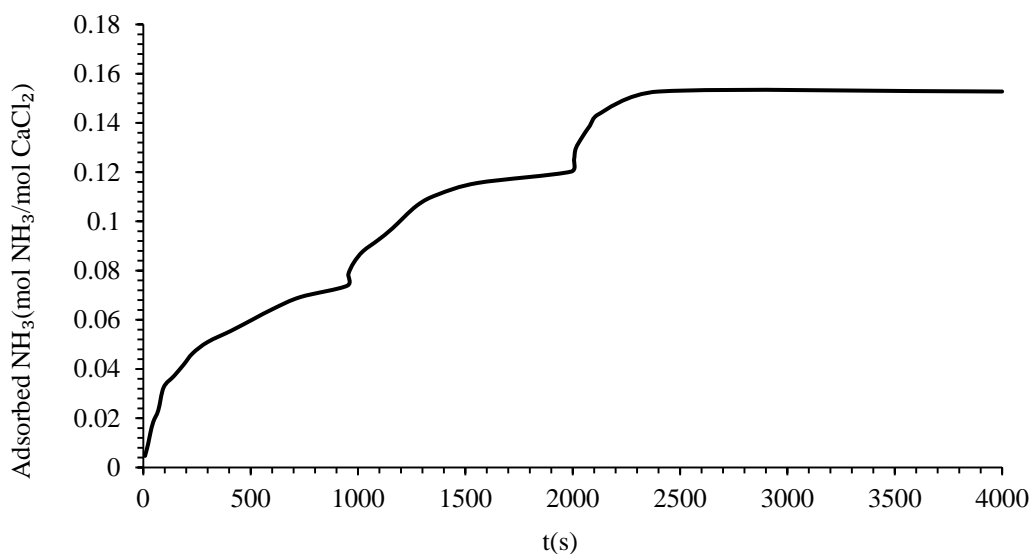
Figure 3.17. Sorbed ammonia on mixture of $ZnCl_2$ -urea DES and reline DES (0.5 : 1 molar ratio).

As it is shown in Figure 3.17, at the end of the third cycle the ammonia sorption onto $ZnCl_2$ -urea DES and reline DES mixture was 0.15 mol NH_3 of ammonia per mole of $CaCl_2$ is sorbed which is much less than than the sorption onto $ZnCl_2$ -urea DES which is 0.36 mol NH_3/ mol $CaCl_2$.

Ammonia sorption into DES samples was also studied by FTIR analyses. For this purpose, the FTIR spectra of ammonia sorbed $ZnCl_2$-urea-$CaCl_2$, $ZnCl_2$ and $CaCl_2$, were compared with the spectra of pure $ZnCl_2$-urea-$CaCl_2$, $ZnCl_2$ and $CaCl_2$. The FTIR spectrum of the samples are given in Figure 3.18.
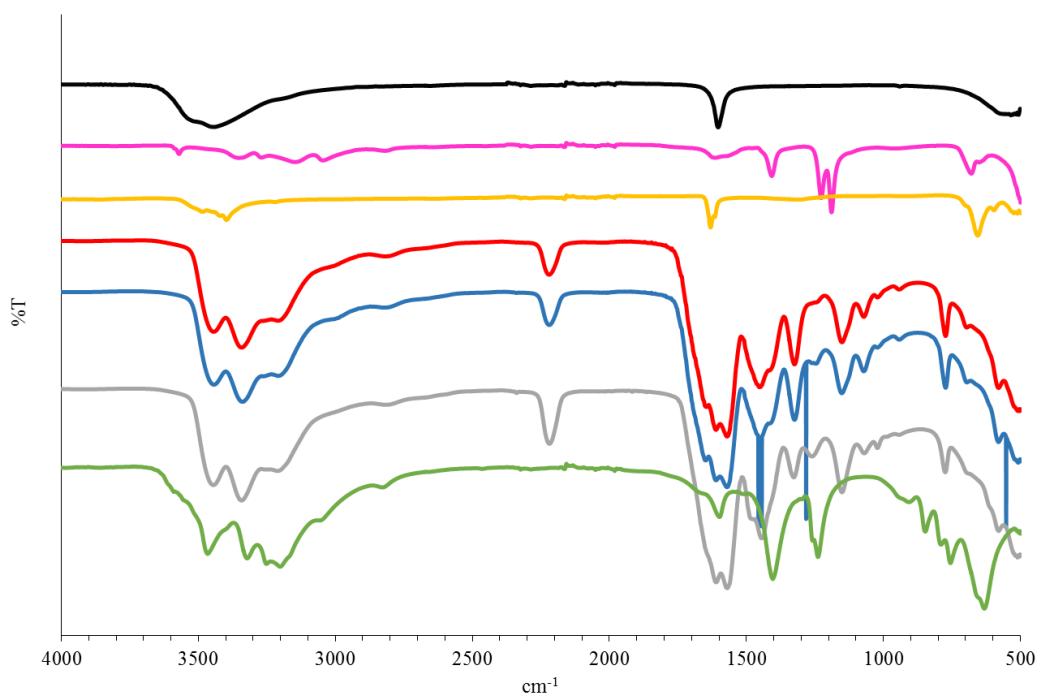
Figure 3.18. FTIR spectra of ammonia sorbed $CaCl_2$, $ZnCl_2$-urea DES-$CaCl_2$ suspension, $ZnCl_2$ and $CaCl_2$, $ZnCl_2$, $ZnCl_2$-urea DES-$CaCl_2$ suspension *(Pink line : ammonia sorbed $CaCl_2$, Yellow line : Pure $CaCl_2$, Blue line : ammonia sorbed $ZnCl_2$-urea DES-$CaCl_2$ suspension, Gray Line :$ZnCl_2$-urea DES, Red Line : $ZnCl_2$-urea DES-$CaCl_2$ suspension, Green line : ammonia sorbed $ZnCl_2$, Black Line: pure $ZnCl_2$)*

Schmidt et al. reported that the stretching vibration of ammonia in the ammonia adsorbed $CaCl_2$ appeared at 3345, 3260 and 3200 cm^{-1} while the bending mode of ammonia appeared at 1590 and 1185 cm^{-1} in their study [71]. Similar peaks were observed ammonia sorbed $CaCl_2$ such as 3045, 3147, 3272 and 1189 cm^{-1}(pink line). Compared to the spectra of $ZnCl_2$-urea DES-$CaCl_2$, in the spectra of ammonia sorbed When $ZnCl_2$ and ammonia adsorbed $ZnCl_2$ were examined, it can be seen that there were new peaks formed at the range between 1500 cm^{-1}– 500 cm^{-1} in ammonia adsorbed $ZnCl_2$ (black and green lines).

3.4.1. Thermal Analyses

Thermogravimetric analyses were carried out in order to evaluate the thermal decomposition of pure $CaCl_2$ and ammonia sorbed $CaCl_2$. Figure 3.16 shows the TGA analyses of the calcium chloride and ammonia sorbed calcium chloride samples showing the mass change with respect to temperature. Pure $CaCl_2$ exhibited very small weight loss and about 3 % mass loss of $CaCl_2$ up to 500°C was observed which can be explained by the amount of adsorbed water and instrumental drift. The mass loss of ammonia sorbed $CaCl_2$ started at the beginning of the analysis. The heat of desorption of ammonia from $CaCl_2$ was calculated from the area under the DTA curve of the ammonia sorbed $CaCl_2$ (Fig 3.19) as 191.5 J/g.
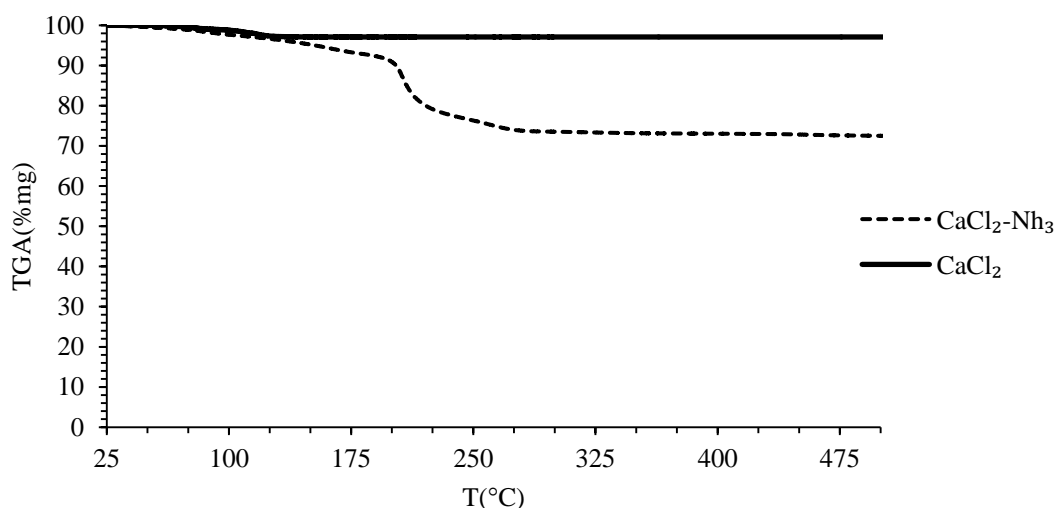
Figure 3.19. TGA analysis of $CaCl_2$ and ammonia sorbed with calcium chloride
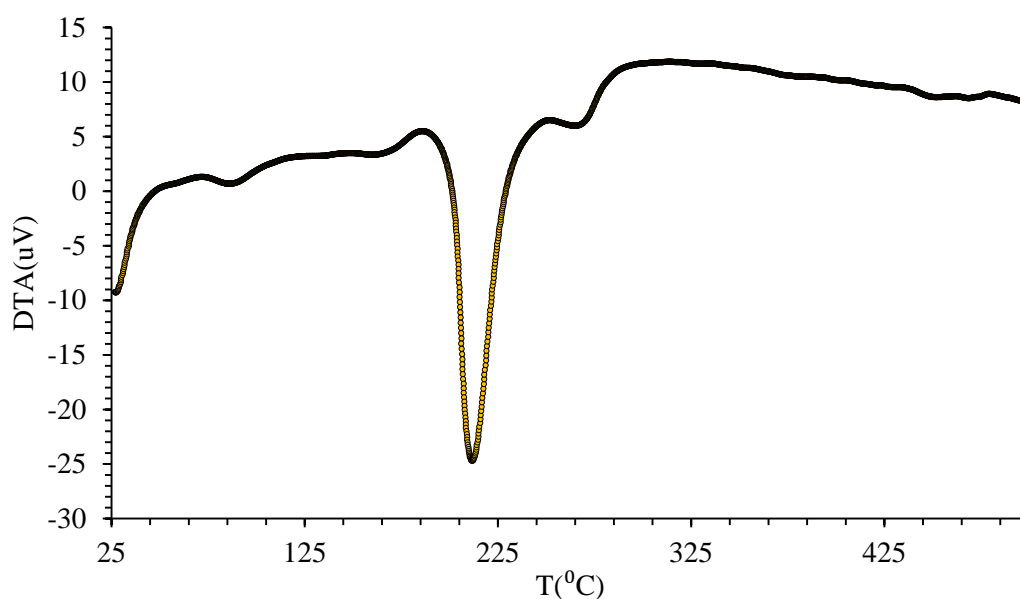
Figure 3.20. Differential thermal analysis (DTA) of ammonia sorbed $CaCl_2$.

TGA analyses of DES-$CaCl_2$ suspension and ammonia sorbed DES-$CaCl_2$ suspension are given in Figure 3.21. The desorption of ammonia which occurs even at room temperature is clearly observed in the TGA thermogram especially above 75 °C, while the DES decomposition starts above 150 °C, which is possibly due to the urea decomposition [72].
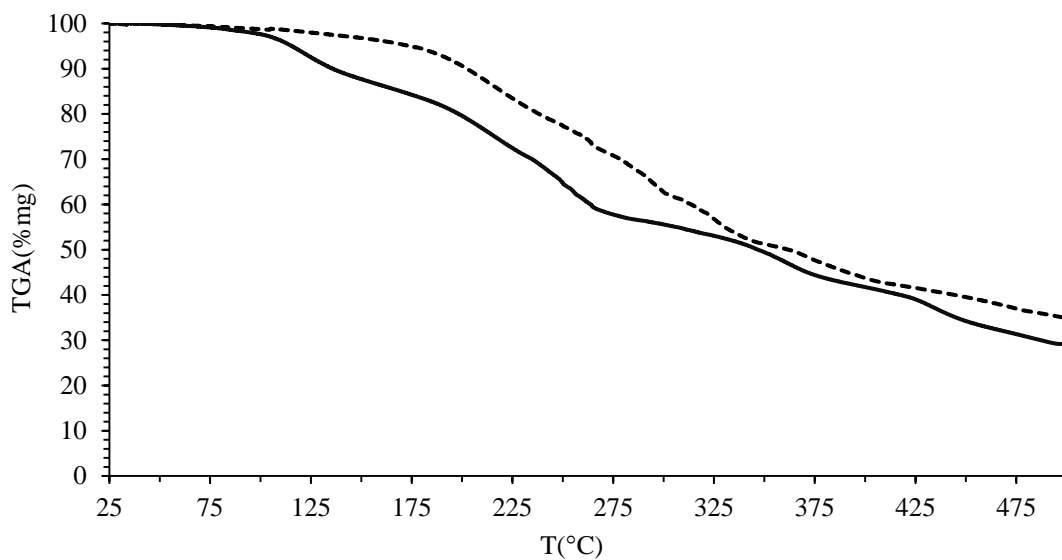
Figure 3.21. TGA analysis of $ZnCl_2$-urea DES-$CaCl_2$ suspension and ammonia sorbed $ZnCl_2$-urea DES-$CaCl_2$ suspension (——$ZnCl_2$-Urea DES-$CaCl_2$+NH_3; - - - - : $ZnCl_2$-Urea DES- $CaCl_2$)
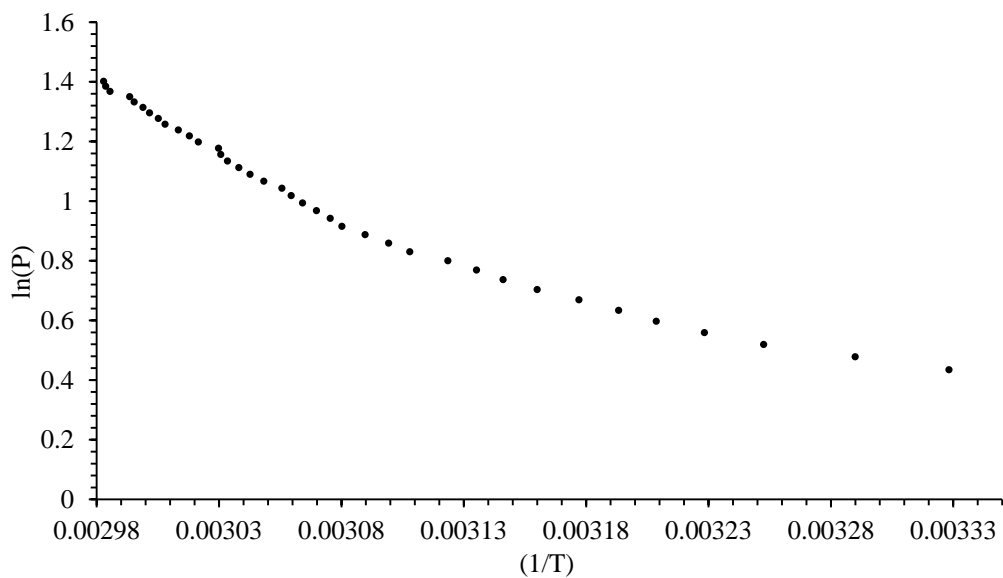
Figure 3.22. ln(P) versus 1/T graph of ammonia desorption from the ammonia-sorbed $CaCl_2$.
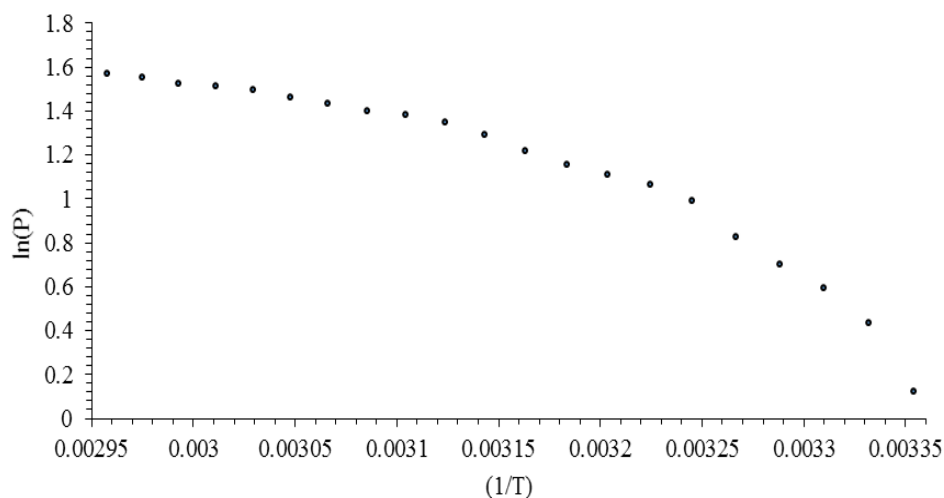
Figure 3.23. ln(P) versus 1/T graph of ammonia desorption from the ammonia-sorbed $ZnCl_2$-urea DES-$CaCl_2$ suspension

In order to observe the desorption behavior of ammonia from pure $CaCl_2$ and $CaCl_2$-$ZnCl_2$-urea samples, the samples at the end of the fifth sorption cycle were heated stepwise from 25°C to 65°C and equilibrium pressure at each temperature were recorded. The heat of desorption of the ammonia was calculated for the ammonia-sorbed pure $CaCl_2$ and ammonia-sorbed $CaCl_2$-$ZnCl_2$-urea DES using the Clausius Clapeyron equation from the equilibrium pressure versus temperature plots of the desorption sorptions (Figures 3.22 and 3.23, respectively). Clausius Clapeyron plot of the date exhibits almost linear trend for pure $CaCl_2$ (Figure 3.23) having the slope corresponding to the heat of desorption of 41.5 kJ/kmol in 55-65 °C temperature range. However, the nonlinear curve was obtained for Clausius Clapeyron plot of the desorption data of $CaCl_2$-$ZnCl_2$-urea sample. The heat of desorption of ammonia over $CaCl_2$-$ZnCl_2$-urea was determined as 51.4 kJ/mol, 20.4 kJ/mol, and 9.4 kJ/kmol at the temperature ranges of 25-35 °C, 35-55 °C, and 55-65 °C, respectively. Which can be assigned to the desorption of ammonia from $CaCl_2$ and $ZnCl_2$. The heat requirement for ammonia desorption decreases as the temperature increases.

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These results show that the use of CaCl$_2$-DES solutions or suspensions is advantageous for heat pump and ammonia absorption processes. ZnCl$_2$ in ZnCl$_2$-urea DES acts as hydrogen bond acceptor as well as sorbent for ammonia. On the other hand, the stability issues of deep eutectic solvents is a major drawback and there is a need to develop new ionic fluids having higher stability for heat pump and absorption applications.

CHAPTER 4

CONCLUSIONS

Chemical heat pumps can provide the ability to capture the rejected low-grade heat and to reuse it at increased temperature levels; therefore, can be preferable in various industrial processes. The pressure and temperature interval of ammonia sorption into $CaCl_2$ is suitable for heat upgrade of waste heat streams, geothermal energy and solar energy sources. The low heat transfer rate in metal salt-ammonia heat pump systems presents the major technical challenge. Metal salts are significantly soluble in ionic solvents and ionic solvents are good reaction mediums. In this study, the potential of the use of deep eutectic solvents as a reaction medium for $CaCl_2$-NH_3 pair was studied. $ZnCl_2$-urea and choline chloride-urea deep eutectic solvents and their physical mixtures were chosen as model solvents. The following conclusions were made at the end of the study.

$ZnCl_2$-urea DES is significantly less stable than choline chloride-urea DES under ambient conditions. The stability of $ZnCl_2$-urea DES depends on the molar ratio of $ZnCl_2$ to urea and varies between 2 to 30 days. However, choline chloride-urea DES is stable for more than six months. However, the physical mixtures prepared by mixing various proportions of two deep eutectic solvents are not stable and phase separation and precipitation were observed within 1 hour.

$CaCl_2$ is significantly soluble in $ZnCl_2$-urea DES at room temperature. $CaCl_2$ solubility depends on the molar ratio of the constituents of the deep eutectic solvent and results showed that solubility of $CaCl_2$ increases with the decreasing molar ratio of $ZnCl_2$ to urea. The solubilities of $CaCl_2$ were determined as 3.7 wt% and 5.3wt% for 3.5:10 and 2.5:10. These results can be explained by the competitive solubility of $CaCl_2$ and $ZnCl_2$ in a liquid phase. However, our control experiments with $CaCl_2$ and

Urea showed that there is no hydrogen bonding between the $CaCl_2$ and urea and no deep eutectic solvent was formed when the mixture of $CaCl_2$ and urea are heated.

Ammonia sorption experiments revealed that the ammonia sorption rate into $CaCl_2$/$ZnCl_2$-urea DES mixture is almost the same with pure solid $CaCl_2$. On the other hand, a higher amount of ammonia is absorbed into $CaCl_2$ $ZnCl_2$-urea DES than solid $CaCl_2$. Our control experiments indicated that ammonia adsorption takes place into both $CaCl_2$ and $ZnCl_2$ and almost no decomposition was observed in deep eutectic solvent. Therefore, $ZnCl_2$ in $ZnCl_2$-urea deep eutectic solvent has two functions and act as a hydrogen bond acceptor and sorbent simultaneously. $ZnCl_2$-urea deep eutectic solvent has a wide range of molar stoichiometric ratios between 3.5:10 to 2.5:10 moles of $ZnCl_2$ to urea and it seems that adsorption of ammonia into the part of $ZnCl_2$ does not cause any decomposition in deep eutectic solvent.

Ammonia sorption experiments with $CaCl_2$ suspensions in choline chloride-urea deep eutectic solvents are also successful and ammonia sorption takes place with a significant rate and extends. However, the sorption rate is significantly slower than the one observed for $CaCl_2$/$ZnCl_2$-urea samples. It is clear that ammonia sorption into dissolved $CaCl_2$ in $ZnCl_2$-urea takes place with a higher rate through gas-liquid mass transfer resistance. However, the sorption reaction of ammonia with $CaCl_2$ in suspension form in choline chloride-urea system is determined and restricted by gas-liquid-solid mass transfer resistances. Therefore the effect of $CaCl_2$ particle size in suspension, mixing and mass transfer surface area on ammonia sorption rate should be studied.

Ammonia sorption experiments with $ZnCl_2$-urea and choline chloride-urea mixture also indicated the significant absorption of ammonia. Although the physical mixtures of two deep eutectic solvents are not stable for a long time, $ZnCl_2$ in the DES mixture absorbs a significant quantity of ammonia with a considerable rate.

The ammonia desorption experiments indicated that ammonia sorption is a completely reversible process. However, the desorption pressure-temperature equilibrium

relationship exhibit a more complex trend than the linear Clausius-Clapeyron equation because of the complex nature of absorption into $CaCl_2$/$ZnCl_2$-urea mixture. The nonlinear behavior of sorption equilibrium can be explained by the desorption of NH_3 from different moieties such as $CaCl_2$, $ZnCl_2$, DES solution.

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APPENDICES

A. ICP Results

Table A. 1. *ICP Results in terms of calcium (Ca)*

$ZnCl_2$-Urea molar ratio	1st Sample Ca (mg/L)	2nd Sample Ca (mg/L)
2.5:10	43	77
3.0 :10	150	45
3.5 : 10	40	77

The amount of solvents used in the dilution process is given in Table A.2.

Table A. 2. *Mass of the mixtures in 100 ml pure water used in ICP analysis*

$ZnCl_2$-urea molar ratio	1st Sample Mixture (g)	2nd Sample Mixture (g)
2.5:10	0.215	0.424
3.0 :10	0.850	0.266
3.5 : 10	0.297	0.557

B. FTIR Results of Upper and Lower Phase
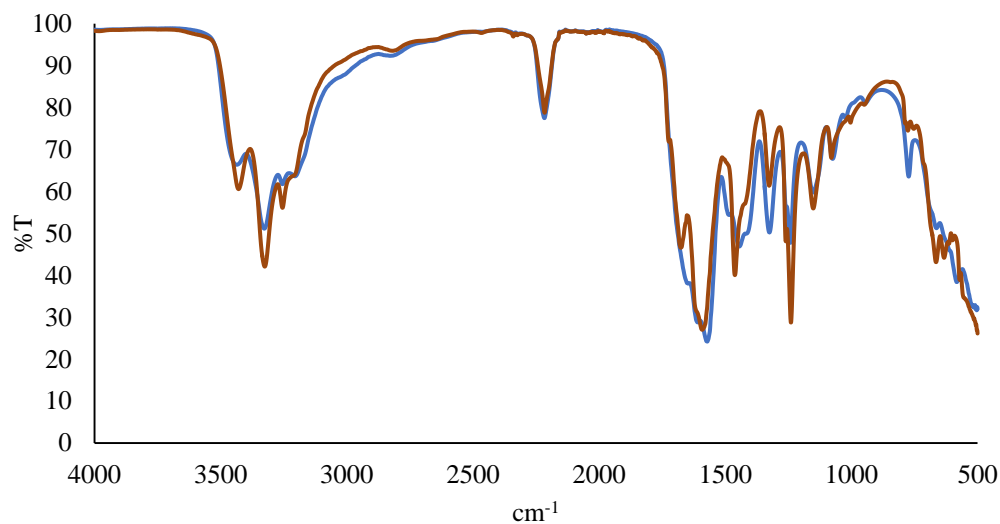
Figure B 1. FTIR spectra upper phase and lower phase of ammonia sorbed $ZnCl_2$ -urea DES and $CaCl_2$ suspension (Blue line:lower phase, Red line:upper phase)

The FTIR spectra of ammonia chemisorbed $ZnCl_2$ -urea DES and $CaCl_2$ was given in Figure B.1. Visually, there a little colour difference between the upper phase and lower phase. The visual difference is given in Figure 3.13. It seems like there were some different bondings but the FTIR spectra do not verify that there is a difference in bonding.

C. Ammonia Sorption Data

Table C. 1. *Ammonia Sorption data for ZnCl₂ -urea DES*

ZnCl₂- Urea DES				
t(s)	N-No(mmol)	N-No(mmol/g ZnCl$_2$)	N-No(mmol/g DES)	N-No(mmol/g urea)
0	0.0000	0.0000	0.0000	0.0000
7	0.1259	0.0639	0.0230	0.0359
11	0.2515	0.1277	0.0459	0.0718
15	0.3767	0.1912	0.0688	0.1075
21	0.4391	0.2229	0.0802	0.1253
29	0.5014	0.2545	0.0916	0.1431
37	0.5637	0.2861	0.1030	0.1609
48	0.6259	0.3177	0.1143	0.1786
62	0.6879	0.3492	0.1257	0.1964
82	0.7498	0.3806	0.1370	0.2140
107	0.8116	0.4120	0.1483	0.2317
136	0.8734	0.4433	0.1596	0.2493
172	0.9350	0.4746	0.1708	0.2669
211	0.9966	0.5059	0.1821	0.2845
266	1.0580	0.5371	0.1933	0.3020
377	1.1194	0.5682	0.2045	0.3195
494	1.1806	0.5993	0.2157	0.3370
668	1.2417	0.6303	0.2268	0.3544
896	1.3029	0.6614	0.2380	0.3719
1220	1.3638	0.6923	0.2491	0.3893
1750	1.4247	0.7232	0.2603	0.4067
1768	1.4878	0.7552	0.2718	0.4247
1773	1.5507	0.7872	0.2833	0.4426
1781	1.6136	0.8191	0.2948	0.4606
1797	1.6763	0.8509	0.3062	0.4785
1814	1.8015	0.9144	0.3291	0.5142
1856	1.8639	0.9461	0.3405	0.5320
1901	1.9262	0.9777	0.3519	0.5498
1999	1.9884	1.0094	0.3633	0.5676
2126	2.0506	1.0409	0.3746	0.5853
2321	2.1126	1.0724	0.3859	0.6030
2570	2.1746	1.1038	0.3973	0.6207
3114	2.2363	1.1352	0.4085	0.6383

Table C.1. *(continued)*

3865	2.2981	1.1666	0.4198	0.6560
5427	2.3598	1.1979	0.4311	0.6736
5447	2.4228	1.2299	0.4426	0.6916
5455	2.4857	1.2618	0.4541	0.7095
5483	2.5486	1.2937	0.4656	0.7275
5658	2.6113	1.3255	0.4770	0.7454
6114	2.7365	1.3891	0.4999	0.7811

Table C. 2. *Ammonia Sorption data for the suspension of ZnCl$_2$ -urea DES and CaCl$_2$*

ZnCl$_2$-Urea DES + CaCl$_2$				
t(s)	N-No(mmol)	N-No(mmol/gCaCl$_2$)	N-No(mmol/gDES)	N-No(mmol/gDES)
0	0.0000	0.0000	0.0000	0.0000
10	0.3963	0.2363	0.0859	0.1342
12	0.5275	0.3146	0.1143	0.1786
15	0.5931	0.3536	0.1285	0.2008
17	0.6585	0.3926	0.1427	0.2230
19	0.7237	0.4316	0.1569	0.2451
24	0.7889	0.4704	0.1710	0.2672
28	0.8539	0.5092	0.1851	0.2892
32	0.9189	0.5479	0.1992	0.3112
36	0.9838	0.5866	0.2132	0.3332
41	1.0485	0.6252	0.2273	0.3551
49	1.1131	0.6638	0.2413	0.3770
58	1.1777	0.7023	0.2553	0.3988
68	1.2421	0.7407	0.2692	0.4206
78	1.3064	0.7790	0.2832	0.4424
91	1.3708	0.8174	0.2971	0.4642
111	1.4349	0.8556	0.3110	0.4859
136	1.4990	0.8938	0.3249	0.5076
156	1.5630	0.9320	0.3388	0.5293
192	1.6268	0.9701	0.3526	0.5509
243	1.6906	1.0081	0.3664	0.5725
303	1.7543	1.0461	0.3802	0.5941
391	1.8179	1.0840	0.3940	0.6156
607	1.8814	1.1219	0.4078	0.6371
610	1.9477	1.1614	0.4221	0.6596

Table C.2. *(continued)*

612	2.2777	1.3582	0.4937	0.7714
617	2.6051	1.5534	0.5646	0.8822
620	2.6703	1.5923	0.5787	0.9043
625	2.7353	1.6310	0.5928	0.9263
630	2.8003	1.6698	0.6069	0.9483
635	2.8651	1.7085	0.6210	0.9703
642	2.9299	1.7471	0.6350	0.9922
651	2.9945	1.7856	0.6490	1.0141
670	3.0591	1.8242	0.6630	1.0360
678	3.1235	1.8625	0.6770	1.0578
697	3.1878	1.9009	0.6909	1.0796
717	3.2522	1.9393	0.7049	1.1014
743	3.3163	1.9775	0.7188	1.1231
790	3.3804	2.0157	0.7326	1.1448
826	3.4443	2.0539	0.7465	1.1664
871	3.5082	2.0920	0.7604	1.1881
932	3.5720	2.1300	0.7742	1.2097
1023	3.6357	2.1680	0.7880	1.2312
1121	3.6993	2.2059	0.8018	1.2528
1310	3.7628	2.2437	0.8155	1.2743
1515	3.8953	2.3228	0.8442	1.3191
1518	4.2248	2.5192	0.9157	1.4307
1520	4.2903	2.5583	0.9299	1.4529
1522	4.4865	2.6753	0.9724	1.5194
1525	4.5516	2.7142	0.9865	1.5414
1529	4.6166	2.7529	1.0006	1.5634
1531	4.6817	2.7917	1.0147	1.5854
1537	4.7465	2.8304	1.0287	1.6074
1542	4.8113	2.8690	1.0428	1.6293
1549	4.8759	2.9075	1.0568	1.6512
1561	4.9405	2.9460	1.0708	1.6731
1568	5.0049	2.9844	1.0847	1.6949
1585	5.0692	3.0228	1.0987	1.7167
1602	5.1336	3.0612	1.1126	1.7385
1627	5.1977	3.0994	1.1265	1.7602
1653	5.2617	3.1376	1.1404	1.7819
1690	5.3257	3.1757	1.1543	1.8036
1731	5.3896	3.2138	1.1681	1.8252

Table C.2. *(continued)*

1786	5.4534	3.2519	1.1819	1.8468
1855	5.5171	3.2898	1.1958	1.8684
1980	5.5807	3.3278	1.2095	1.8899
2158	5.6442	3.3656	1.2233	1.9114
2354	5.9088	3.5234	1.2806	2.0010
2356	6.1717	3.6802	1.3376	2.0900
2360	6.4330	3.8360	1.3943	2.1785
2361	6.4980	3.8748	1.4084	2.2006
2362	6.5630	3.9136	1.4224	2.2226
2363	6.6279	3.9522	1.4365	2.2445
2368	6.6927	3.9909	1.4505	2.2665
2371	6.7573	4.0294	1.4645	2.2884
2376	6.8219	4.0679	1.4786	2.3102
2382	6.8862	4.1063	1.4925	2.3320
2392	6.9506	4.1447	1.5064	2.3538
2401	7.0149	4.1830	1.5204	2.3756
2418	7.0790	4.2213	1.5343	2.3973
2438	7.1431	4.2595	1.5482	2.4190
2472	7.2071	4.2976	1.5620	2.4407
2512	7.2710	4.3357	1.5759	2.4623
2586	7.3348	4.3737	1.5897	2.4839
2648	7.3985	4.4117	1.6035	2.5055
2704	7.4620	4.4496	1.6173	2.5270
2967	7.5255	4.4875	1.6311	2.5485
3558	7.5919	4.5270	1.6454	2.5710
3559	7.9219	4.7238	1.7170	2.6827
3563	8.1840	4.8801	1.7738	2.7715
3565	8.3794	4.9967	1.8161	2.8377
3568	8.4444	5.0354	1.8302	2.8597
3570	8.5093	5.0741	1.8443	2.8817
3572	8.5740	5.1127	1.8583	2.9036
3574	8.6387	5.1513	1.8723	2.9255
3580	8.7033	5.1898	1.8863	2.9474
3585	8.7676	5.2282	1.9003	2.9692
3600	8.8320	5.2665	1.9142	2.9910
3608	8.8963	5.3049	1.9282	3.0127
3624	8.9604	5.3431	1.9420	3.0345
3647	9.0245	5.3813	1.9559	3.0562

Table C.2. *(continued)*

3680	9.0885	5.4195	1.9698	3.0778
3727	9.1524	5.4576	1.9837	3.0995
3794	9.2162	5.4956	1.9975	3.1211
3880	9.2798	5.5336	2.0113	3.1426
4020	9.3434	5.5715	2.0251	3.1642
4267	9.4069	5.6094	2.0388	3.1857
5250	9.4069	5.6094	2.0388	3.1857

Table C.3. *Ammonia sorption data for ZnCl$_2$*

ZnCl$_2$		
t(s)	N-No(mmol)	N-No(mmol/gZnCl$_2$)
0	0.0000	0.0000
5	0.1502	0.0531
8	0.2252	0.0796
12	0.2999	0.1060
15	0.4492	0.1587
17	0.5236	0.1850
20	0.5978	0.2112
23	0.6721	0.2375
32	0.7462	0.2637
36	0.8202	0.2898
45	0.8940	0.3159
51	0.9677	0.3419
70	1.0414	0.3679
82	1.1149	0.3939
95	1.1882	0.4198
99	1.2615	0.4457
115	1.3347	0.4716
139	1.4076	0.4973
165	1.4806	0.5231
180	1.5535	0.5489
203	1.6261	0.5745
252	1.6987	0.6002
305	1.7713	0.6258
390	1.8437	0.6514
563	1.9159	0.6769

Table C.3. *(continued)*

960	1.9881	0.7024
986	2.0633	0.7290
1007	2.1383	0.7555
1052	2.2133	0.7820
1110	2.2880	0.8084
1189	2.4373	0.8611
1260	2.5117	0.8874
1350	2.5859	0.9137
1517	2.6602	0.9399
2745	2.8821	1.0183
2757	2.9573	1.0449
2801	2.9571	1.0448
2848	2.9571	1.0448
2951	2.9568	1.0447
6349	3.3284	1.1760
6374	3.4036	1.2026
6565	3.4035	1.2025
7364	3.4035	1.2025
9063	3.4032	1.2024
9088	3.4783	1.2290
9663	3.4782	1.2289

Table C. 4. *Ammonia sorption data for urea*

Urea		
t(s)	N-No(mmol)	N-No(mmol/gNH₃)
0	0.0000	0.0000
28	0.0848	0.0221
45	0.1695	0.0442
74	0.2541	0.0663
94	0.3385	0.0883
130	0.5069	0.1322
180	0.5909	0.1541
350	0.6748	0.1760
694	0.7586	0.1979
1524	0.8422	0.2197
1617	1.0107	0.2197