Advanced NH$_3$ based absorption refrigeration cycles
Modelling of the ionic liquid based double-effect cycles
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4051009
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Modelling of the ionic liquid based double-effect cycles

by

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Preface

Firstly, I would like to thank my supervisor Dr. ir. C.A. Infante Ferreira for his continuous support and encouragement of my thesis project. His help and patience were very important during my graduation period.

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Bob Schouten
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Absorption refrigeration cycles are energy saving as they can be driven by waste heat instead of electricity. By doing so, they reduce the use of fossil fuels, resulting in a reduction of emissions. However, many challenges exist for the traditional working fluids of the cycle, such as the crystallization problem of the water-lithium bromide pair and the difficulty in separating ammonia from the ammonia-water working pair. Ionic liquids, as novel absorbents in absorption cycles, have attracted considerable attention because of their unique properties like negligible vapor pressure, negligible flammability, thermal stability, low melting temperatures, liquid state over a wide temperature range and good solubility.

In this thesis, a thermodynamic model of the ammonia based double-effect absorption cycle in series configuration was used to predict the performance and suitability of nine ionic liquids as potential absorbents. The performance of the ammonia-ionic liquid systems was compared with that of ammonia-water systems and the influence of the operating conditions and the design parameters on the performance was investigated.

Furthermore, a method to experimentally determine the excess enthalpy of ammonia and ionic liquid mixtures is proposed and the suitability of using absorption refrigeration on a fishing ship, with ionic liquids as absorbents, is studied.

The results show that the ionic liquids [Bmim][BF4], [Mmim][DMP] and [Emim][SCN] used as absorbents in the investigated absorption cycle reached the best performance and could be a promising replacement of water in the ammonia-water working pair. The best performing ionic liquid, [Bmim][BF4], was found to be a better performing absorbent than water in the double-effect cycle.
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## Nomenclature

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>[Bmim][BF4]</td>
<td>1-butyl-3-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>[Bmim][PF6]</td>
<td>1-butyl-3-methylimidazolium hexafluorophosphate</td>
</tr>
<tr>
<td>[Emim][BF4]</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>[Emim][EtOSO3]</td>
<td>1-ethyl-3-methylimidazolium ethylsulfate</td>
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<td>[Emim][SCN]</td>
<td>1-ethyl-3-methylimidazolium thiocyanate</td>
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<tr>
<td>[Emim][Tf2N]</td>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
</tr>
<tr>
<td>[Hmim][BF4]</td>
<td>1-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>[Mmim][DMP]</td>
<td>1,3-dimethylimidazolium dimethyl phosphate</td>
</tr>
<tr>
<td>[Omim][BF4]</td>
<td>1-methyl-3-octylimidazolium tetrafluoroborate</td>
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<tr>
<td>ABS</td>
<td>Absorber</td>
</tr>
<tr>
<td>CON</td>
<td>Condenser</td>
</tr>
<tr>
<td>COP</td>
<td>Coefficient of performance</td>
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<tr>
<td>CWP</td>
<td>Chilled water plant</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
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<tr>
<td>EOS</td>
<td>Equation of state</td>
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<tr>
<td>EVA</td>
<td>Evaporator</td>
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<tr>
<td>GAX</td>
<td>Generator absorber heat-exchange</td>
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<tr>
<td>HEX1</td>
<td>Heat exchanger 1</td>
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<tr>
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<td>Heat exchanger 2</td>
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<td>High pressure generator</td>
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<td>Intermediate pressure generator</td>
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<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<td>NRTL</td>
<td>Non random two liquid</td>
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<td>Rectifier 1</td>
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<tr>
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<td>Rectifier 2</td>
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<tr>
<td>RMSD</td>
<td>Root-mean-square deviation</td>
</tr>
<tr>
<td>RR</td>
<td>Reflux ratio</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>$\Delta T$</td>
<td>Temperature rise [K]</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass flow rate [kg/s]</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>Rate of heat transfer [J/s]</td>
</tr>
<tr>
<td>$\dot{W}$</td>
<td>Power [J/s]</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat capacity [J/kg/K]</td>
</tr>
<tr>
<td>$dT$</td>
<td>Temperature difference between flows [K]</td>
</tr>
<tr>
<td>$L$</td>
<td>Length [m]</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass [kg]</td>
</tr>
<tr>
<td>$M^E$</td>
<td>Excess property [−]</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure [Pa]</td>
</tr>
<tr>
<td>$Q$</td>
<td>Heat transferred [J]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature [K/°C]</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume [m$^3$]</td>
</tr>
<tr>
<td>$x$</td>
<td>Mass concentration of the refrigerant in the liquid phase [kg/kg]</td>
</tr>
<tr>
<td>$y$</td>
<td>Mass concentration of the refrigerant in the vapor phase [kg/kg]</td>
</tr>
<tr>
<td>$\bar{h}^E$</td>
<td>Specific mole based excess enthalpy [J/mole]</td>
</tr>
<tr>
<td>$h^E$</td>
<td>Specific mass based excess enthalpy [J/kg]</td>
</tr>
<tr>
<td>$h$</td>
<td>Specific mass based enthalpy [J/kg]</td>
</tr>
</tbody>
</table>

**Super- and subscript**

1, 2, ... State indicator  
$a, b, ...$ Indicator of component in mixture  
box Experimental insulated box  
calc Calculated value  
cooling For a cooling application  
dec Decomposition  
ex Exhaust gas  
exp Experiment  
guess Guess value  
$H_2O$ Water component  
heating For a heating application
List of Figures

\[ i \] Species of the \( i \)-t component

\[ id \] Ideal mixture

\[ in \] Inlet

\[ l \] Liquid phase

\[ max \] Maximum

\[ min \] Minimum

\[ mix \] Mixing

\[ NH_3 \] Ammonia component

\[ out \] Outlet

\[ PUMP \] Solution pump

\[ rec \] Recovered

\[ rel \] Released

\[ samp \] Experimental connected sample

\[ sat \] Saturated condition

\[ sea \] Seawater

\[ sol \] Solution

\[ tot \] Total

\[ v \] Vapor phase

\[ IL \] Ionic liquid

**Greek letter**

\[ \alpha \] Parameter in NRTL model [−]

\[ \gamma \] Activity coefficient [−]

\[ \tau \] Parameter in NRTL model [−]

\[ \rho \] Density [kg/m³]

\[ \eta \] Efficiency [−]
1.1. Background

Nowadays, problems like global warming and pollution are increasingly standing out. The need for energy-saving and green technology is urgent. Absorption refrigeration and absorption heat pumps are energy-saving as they can be driven by solar power or waste heat making them promising technologies [30]. Additionally, they can use working fluids with zero "ozone depletion" and "global warming potential" fulfilling both the Montreal Protocol and the Kyoto Protocol [3]. Therefore, they have attracted much attention as a real alternative to traditional electricity consuming vapor-compression cycles [15, 40].

However, many challenges exist for the traditional working pairs, such as the crystallization problem of the water and lithium bromide pair when operating temperature is high and the difficulty in separating ammonia from the ammonia and water working pair [39]. New ionic liquids are being investigated for their potential roles in replacing the absorbents in traditional working pairs [1].

Ionic liquids are salts that remain in liquid state at near or below room temperature. In recent years, ionic liquids have attracted considerable attention because of their unique properties, e.g. negligible vapor pressure, negligible flammability, thermal stability, low melting temperatures, liquid state over a wide temperature range and good solubility [4, 6, 9, 27]. Therefore, absorption systems which make use of working pairs that include ionic liquids have been investigated.

Unfortunately, for the ammonia and ionic liquid systems, experimental heat capacity and mixing enthalpy data, which are critical for the evaluation of thermodynamic processes, have only scarcely been reported. Since ammonia based absorption systems are suitable for sub-zero degree applications and are free of air infiltration (they operate above atmospheric pressure), ammonia and ionic liquid working pairs could be very promising as working fluids for heat driven thermodynamic cycles.

1.2. Literature review

1.2.1. Absorption refrigeration and absorption heat pumps

Absorption technology, which is the focus of this thesis, is an example of a heat-driven technology. The simplest and most common heat-driven heat pump is a device that transfers heat at three temperature levels, as shown in figure 1.1. In this type of heat pump, the driving heat is delivered at the
1. Introduction

Figure 1.1: Temperature levels of a simple absorption heat pump or absorption refrigeration system. When the cycle is used for a cooling application, the cooling load is supplied at the lowest temperature level ($T_C$). For heating applications, the heat is delivered at the intermediate temperature level ($T_I$).

The product is either refrigeration at the lowest temperature ($T_C$) or heating at the intermediate temperature ($T_I$). The single-effect absorption cycle is the most basic example operating at three temperature levels which is explained later in this section. Other heat-driven technologies that have been demonstrated include adsorption and Stirling cycle refrigeration [13].

Configurations of absorption cycles Absorption cycles have many different configurations including the single effect cycle, double effect cycle, double lift cycle, GAX cycle and other cycles [26]. Except for the single effect cycle, other cycles are proposed for high efficiency, high temperature lift or strong flexibility [35]. For example, the double effect cycle has a high COP, the double lift cycle has high temperature lift and the GAX cycle has stronger flexibility. All of the discussed configurations have an important feature in common, they all re-use heat within the cycle. This is referred to as “internal heat exchange”. The most basic example of a device that utilizes internal heat is the solution heat exchanger. The single-effect cycle shown in figure 1.2 employs such a heat exchanger.

Single-effect absorption cycle Figure 1.2 shows the standard heat driven single effect absorption cycle (right) and the mechanical vapor-compression refrigeration cycle (left). They are two of the most basic and commonly used refrigeration cycles. Both the mechanical vapor-compression cycle and the absorption cycle make use of a condenser, valve and evaporator to supply the cooling power. However, the main difference between the two systems is the method used to compress the refrigerant vapor from the low pressure level to the high pressure level.

In the mechanical vapor compression refrigeration cycle a compressor is used to increase the pressure level of the refrigerant by using mechanical work, and thus, electricity. In contrast, with respect to the single-effect absorption cycle, the compressor is replaced by an absorber, generator, throttling valve and a solution pump. The combination of these components can be interpreted as a “thermal compressor” (see the dashed box in figure 1.2) as it uses heat as input instead of mechanical power to compress the refrigerant. Furthermore, a suitable working fluid that is able to absorb and desorb the refrigerant at certain temperatures and pressures is required to ensure effective operation.

During the thermal compression process, the refrigerant at the lowest pressure level coming from
the evaporator enters the absorber where it is absorbed into a liquid solution to form a strong solution (strong in refrigerant). During this absorption process, the refrigerant condenses. After that, the strong solution is pumped from the low pressure level to the high pressure level after which it enters the generator, where the solution absorbs heat from a high temperature heat source to desorb the refrigerant. In most single-effect absorption cycles, a solution heat exchanger is deployed between the generator and the absorber in order to use the heat from the hot solution leaving the generator to pre-heat the cold solution coming from the absorber. By doing so, the solution heat exchanger reduces the heat required by the generator to desorb the refrigerant and the cooling power required by the absorber to condens and absorb the refrigerant. The major advantage of the thermal compressor compared to the mechanical compressor is that it needs much less mechanical power to boost the pressure of the refrigerant. Instead of mechanical power, the thermal compressor uses a heat input in the generator from a temperature that is greater than the ambient temperature. Single effect absorption chillers are marketed products. Companies including Broad, Carrier, Colibri, Mitsubishi, Robur, Sanyo, Trane, York and some other companies all have business on single-effect water–lithium bromide chillers or single-effect ammonia– water chillers [13].

Double-effect effect absorption cycle The single-effect absorption system has a relatively low COP due to which it is not competing economically with the conventional vapor compression system, except in case of waste heat applications where the input energy is virtually free of cost. To reduce operating cost of the absorption cycle, it is desirable to increase the COP. Therefore, multi-effect absorption systems with high temperature heat sources have now been developed [2].

Figure 1.3 shows a simplified process flow diagram of a double-effect absorption cycle in series configuration. The cycle makes use of "internal heat exchange" in a couple of ways. The condensation–generation coupling increases the cycle efficiency by using condensation heat from the vapor in the high pressure condenser to generate vapor in the intermediate pressure generator. At the same time, the driving temperature and system pressure are increased.

When the heat source temperature increases, the COP of a single effect cycle only stays stable. In order to make better use of the heat input, the condensation–generation heat coupling is used to form a new cycle, as shown in figure 1.3 in the dashed box.

Series, parallel or reverse configurations can be adopted for the solution flow. In the series flow configuration, the solution from the absorber flows into the high pressure generator and intermediate
Figure 1.3: Process flow diagram of the double-effect absorption cycle in a series configuration. The red, blue and purple lines indicate the strong, intermediate and weak solution flows respectively. The green lines indicate the refrigerant flow. The dotted lines indicate the vapor phase and the solid lines indicate the liquid phase.

pressure generator successively. In the parallel flow configuration, the solution from the absorber flows into the high pressure generator and the intermediate pressure generator at the same time. In the reverse flow configuration, the solution from the absorber first flows into the intermediate pressure generator and then into the high pressure generator [35].

Herold et al. [13] presented the cooling capacities of different solution flow configurations for the double-effect absorption cycle from simulation. The cooling capacities of series, parallel and reverse configurations were investigated and series flow was found to have the highest capacity. Because of this, series flow will be investigated in present research.

Traditional working pairs The most common working pairs for absorption systems are lithium bromide-water and ammonia-water. Lithium bromide–water based absorption systems are widely used for their high efficiency. This working pair utilizes water as refrigerant and is therefore limited to evaporation temperatures above 0 °C. Absorption cycles based on this working pair are typically configured as water chillers for air-conditioning systems in large buildings. They have a reputation as consistent and dependable. The COP typically varies over the range 0.7 < COP < 1.2. Single-effect lithium bromide–water systems are manufactured and sold throughout the world. Single-effect machines are typically fired indirectly with heat coming from steam or hot water at temperatures above 75 °C and with COPs around 0.7. Double-effect lithium bromide-water systems are also manufactured by multiple companies. The COP of these double-effect systems typically varies from 1.0 to 1.2 [13].

The ammonia–water absorption chiller is popular for no danger of crystallization and the ice-making ability. Besides, the wide concentration range of ammonia–water allows heat recovery through
generator-absorber heat exchange (GAX). This working pair utilizes ammonia as the refrigerant. One advantage of ammonia as refrigerant is that the allowable refrigeration temperature is very low (the freezing temperature of ammonia is \(-77.7 \, ^\circ\text{C}\)). Single-stage ammonia-water systems have been in use for a long time \([13]\).

Ammonia is a colorless gas of low density (lower than air) at room temperature with a pungent smell. It is widely used for agriculture as fertilizer and source material for fibers, plastics, explosives and cleaning agents. It can be transported as a liquid under a pressure of \(1 \, \text{MPa}\) and at \(25 \, ^\circ\text{C}\). The critical point of ammonia is at \(132.2 \, ^\circ\text{C}\) and \(11.3 \, \text{MPa}\). The strong odor can be seen as an asset. Even very small leaks are easily noticed and therefore a significant incentive exists for early repairs and consistent maintenance. Compared to lithium bromide-water systems, operating pressures are higher. This is because the boiling point at atmospheric pressure of ammonia is \(-33.35 \, ^\circ\text{C}\), compared to \(100\, ^\circ\text{C}\) for water. A second important difference is that the vapor pressure of water (the absorbent) is not negligible relative to that of ammonia. As a consequence, vapor generated in the generator contains a certain amount of water. Any water contained in the vapor leaving the generator is harmful to the performance of the system. The water will pass with the vapor into the condenser and then into the evaporator where the water tends to accumulate. Accumulation of water in the evaporator will lead to a decrease in evaporator pressure which in turn, affects the absorber conditions because they operate at the same pressure. One way of preventing excessive water accumulation in the evaporator is to drain it into the absorber. However this method harms the performance of the system in two ways. First, the water was evaporated in the generator, requiring heat input, but it does not evaporate in the evaporator, so it does not provide cooling capacity. Second, the water accumulated in the evaporator contains an amount of ammonia that is, consequently, not evaporated amplifying this effect. To prevent this, a rectifier can be added. Figure 1.4 shows a single-effect cycle that employs a rectifier. The water containing vapor leaves the desorber (generator) and flows into the rectifier. The rectifier exchanges heat with the environment cooling down the vapor, causing most of the water to condens. The water will flow back into the generator as reflux preventing the accumulation of water in the evaporator. Because of this undesired evaporated water, the generator requires more heat input which decreases the performance.

Concluding, for the same application, lithium bromide-water is more efficient than ammonia-water. The reasons are hidden in the fluid properties. As explained before, because ammonia-water needs a rectifier the efficiency goes down. Furthermore, the specific heat of ammonia-water is about twice as large as lithium bromide-water. Thus, any inefficiency of the solution heat exchangers causes a large penalty in ammonia-water systems. Lastly, the latent heat of ammonia is about half as large as that of water. Thus, for the same cooling capacity in the evaporator, a larger refrigerant flow is required.

### 1.2.2. Methods to measure excess enthalpies

Diffusivities, heat capacities and solubilities of various ionic liquid mixtures have been studied \([1, 4, 6, 9, 27, 29]\). Then, very high solubilities were found which led researchers to think of several applications with ionic liquid mixtures. One of the proposed applications was for absorption cycles. The feasibility of ammonia absorption cycles, using ionic liquids as absorbents, was investigated and very high solubilities were found \([37]\). Also the experimental PTx-data have successfully been correlated with an equation of state (EOS) model which has been used to calculate excess properties \([36]\). According to that study, the properties of the ammonia ionic liquid mixtures show promise for replacing the traditional ammonia water working pair for absorption cycle applications.

Different methods have been demonstrated for measuring various properties of ionic liquid mixtures. Excess enthalpies of ionic liquids with short-chain alcohols, e.g. ethanol and propanol, have
1. Introduction

The rectifier is used to remove water from the vapor steam leaving the desorber in order to prevent water accumulation in the evaporator [13].

Other methods include the use of static phase equilibrium cells [36]. It is important to know whether mixing processes between ammonia and water are exothermic, because this is a necessary property for the absorption cycle.

1.3. Research objectives

The main objective of this thesis is to analyze the performance of the double-effect absorption cycle in series configuration using ionic liquid-ammonia working pairs and to compare them with the ammonia-water working pair. Further objectives are to develop a method to experimentally determine the mixing enthalpy of ammonia ionic liquid mixtures and to investigate the suitability of absorption refrigeration, using an ionic liquid as absorbent, on a fishing ship for the refrigeration of fish.

1.4. Thesis outline

- Chapter 2 describes the thermodynamic model of a double-effect absorption cycle with two rectifiers in series configuration with ammonia and water as working pair. The influence of the operating conditions and the design parameters is investigated.
- Chapter 3 uses the thermodynamic model described in chapter 2, without the rectifiers, to predict the performance and suitability of nine ionic liquids as absorbents using ammonia as refrigerant.
- Chapter 4 proposes a method to measure the mixing enthalpy of ammonia and ionic liquid mixtures using samples.
- Chapter 5 describes a case-study of a Dutch trawler fishing vessel and the opportunity to use
[Bmim][BF4] and ammonia as working pair for the double-effect absorption cycle on board for the refrigeration fish.

- Chapter 6 presents the conclusions and outlook
Double-Effect absorption system with ammonia-water

2.1. Introduction

This chapter describes the mathematical model to calculate thermodynamic processes of a double-effect absorption cycle using ammonia and water as working pair. The performance and limitations of the cycle under different operating conditions are investigated. A modification of the model is used in chapter 3 to do the same investigation for ammonia and ionic liquid working pairs. Firstly, the thermodynamic model of the double-effect ammonia-water absorption cycle in series configuration will be described in detail. The boundaries, the individual components within the system, the assumptions of the model, and the formulation of the mathematical equations are presented. Then, the results obtained by the thermodynamic model are discussed and the behaviour of the model is analysed. Lastly, the influence of the design parameters on the performance of the cycle is investigated and the conclusions are presented.

2.2. Thermodynamic model

2.2.1. Cycle description

A process flow diagram of the double effect absorption cycle in series configuration is shown in figure 2.1. The main components of this cycle are the high pressure generator (HPG), the intermediate pressure generator (IPG), the high pressure condenser (HPC), the condenser (CON), the absorber (ABS), the evaporator (EVA), two rectifiers (REC1 and REC2) and two solution heat exchangers (HEX1 and HEX2). The main difference with a traditional double effect series cycle is the addition of two rectifiers because the ammonia rich vapor coming from the high pressure generator and the intermediate pressure generator (streams 11a and 14a) has to be purified. If these streams do not get purified, water may build up in the evaporator which could cause the system to fail.

A qualitative illustration of the temperature and pressure relationship of each state is illustrated in figure 2.2. The diagram shows the relation between the three pressure levels and temperatures in the evaporator, absorber, condenser and high pressure generator. The diagonal lines are constant concentration lines. The lowest pressure level ($P_{EVA}$) is determined by the evaporation temperature of the pure ammonia, which is displayed by the green diagonal line. The strongest solution concentration ($x_4$) is determined by the intersection between the absorber outlet temperature and the lowest pressure level.
Figure 2.1: Process flow diagram of the double-effect absorption cycle in a series configuration. The red, blue and purple lines indicate the solution of the weak, intermediate and strong concentration. Green lines indicate the refrigerant flows. The dotted lines indicate the vapor phase and the solid lines indicate the liquid phase. The grey arrows indicate where the exchange of heat takes place.

Figure 2.3 shows how the double-effect absorption cycle interacts with the environment when it is used for a cooling application, for example making ice or the air conditioning of a building. The cooling demand \( \dot{Q}_{\text{EVA}} \) is supplied by the evaporator, where ammonia gets evaporated at the lowest pressure \( (P_{\text{EVA}}) \) and temperature level \( (T_{\text{EVA}}) \). The absorber rejects heat to the environment \( (\dot{Q}_{\text{ABS}}) \) to condense ammonia and absorb it into the solution. Similarly, the condenser rejects heat to the environment while condensing ammonia at the intermediate pressure level \( (P_{\text{CON}}) \). Usually, the absorber and condenser exchange heat with water or air from the environment at ambient temperature. At the highest pressure level \( (P_{\text{HPG}}) \), the high pressure generator absorbs heat \( (\dot{Q}_{\text{HPG}}) \) from an external source to evaporate ammonia from the solution. Furthermore, the pump uses power \( (\dot{W}_{\text{PUMP}}) \) to pump the solution around. To study the performance of the cycle during a cooling application the coefficient of performance (COP) is used which can be calculated with equation 2.1.

\[
\text{COP}_{\text{cool}} = \frac{\dot{Q}_{\text{EVA}}}{\dot{Q}_{\text{HPG}} + \dot{W}_{\text{PUMP}}} \tag{2.1}
\]

Figure 2.4 shows how the cycle interacts with the environment when it is used for a heating application. The heating of the application, for example the heating of a building, takes place at multiple components. Because the ammonia vapor leaving the low and high pressure generators has to be
rectified, more heat is rejected to the environment. This extra heat can be used to increase the performance. The COP of the cycle when it used for a heating application is calculated with equation 2.2.

\[
\text{COP}_{\text{heat}} = \frac{\dot{Q}_{\text{ABS}} + \dot{Q}_{\text{CON}} + \dot{Q}_{\text{REC1}} + \dot{Q}_{\text{REC2}}}{\dot{W}_{\text{HPG}} + \dot{W}_{\text{PU MP}}} \quad (2.2)
\]

In order to represent and simplify the physics of the double-effect absorption cycle, the following assumptions are made:

- The system operates at steady state
- The pressure drop due to friction in the pipelines and the heat exchangers of the system is negligible
- All components are well insulated and the heat losses to the surrounding are negligible
- The refrigerant at the outlet of the condenser is saturated liquid
- The solution at the outlet of the evaporator is saturated vapor
- At the exit of the absorber and the generators, the solutions are at equilibrium conditions
- The vapor outlets of the rectifiers are 30 K superheated
- The solution outlets of the rectifiers are at saturation conditions, 20 K lower than the vapor outlet temperatures.
- The vapor outlets of the rectifiers have a minimum purity of 99.9%
- The vapor outlets of the high pressure generator and the intermediate pressure generator have the same temperature as the respective strong solution inlet
- The pinch temperatures of HEX1, HEX2 and the intermediate pressure generator are 5 K
Double-effect absorption system with ammonia-water

![Diagram](image)

Figure 2.3: Boundary of the double effect absorption system when it is used for cooling. The red dotted line displays the boundary of the system, the heat flows and power demand used to calculate the COP are displayed for the different components.

The cycle operates at three different pressure levels, as can be seen figure 2.2. These can be determined by using the operating conditions $T_{EVA}$, $T_{ABS}$, $T_{CON}$ and $T_{HPG}$. The absorber and the evaporator operate at the lowest pressure level $P_{EVA}$. This pressure level can be determined by the temperature of the evaporator because we know the composition of the saturated stream leaving the evaporator. With these properties the pressure can be determined from NIST’s REFPROP database [17]. The condenser and second rectifier operate at the intermediate pressure level $P_{CON}$. This pressure level can be determined from the condenser temperature $T_{CON}$ and the composition which has been imposed. With $P_{EVA}$ and $T_{ABS}$ the concentration of the ammonia rich stream leaving the absorber can be determined. This concentration remains unchanged until it reaches the high pressure generator.

The highest pressure level, $P_{HPG}$, is determined by the outlet temperature ($T_{12}$) of the intermediate pressure generator. With $P_{HPG}$ and $T_{HPG}$ the concentration of the ammonia lean solution leaving the high pressure generator can be determined giving the concentration of state points 8, 9 and 10. To calculate all the other points, heat balances, mass balances and species balances are used. These balances are calculated for each component as follows:

**Solution pump** To calculate the work done by the pump we assume a pump efficiency $\eta_{PUMP}$ and use the following equations. A mass flow of 1 kg/s is assumed, this can always be changed to match the desired heating or cooling demand.

$$\dot{m}_4 = \dot{m}_5$$ (2.3)

$$W_{pump} = \frac{\dot{m}_5 P_{HPG} - P_{EVA}}{\rho_{sol} \eta_{PUMP}}$$ (2.4)

**High pressure generator and the first rectifier** Heat is supplied to the high pressure generator in order to evaporate ammonia from the solution. This vapor goes to the rectifier which sends a part of this back to the high pressure generator as reflux. The ammonia lean solution exits the high
2.2. Thermodynamic model

Double-effect absorption cycle

Heating demand
\( \dot{Q}_{\text{CON}} + \dot{Q}_{\text{ABS}} + \dot{Q}_{\text{REC1}} + \dot{Q}_{\text{REC2}} \)

Heat source
\( \dot{Q}_{\text{HPG}} \)

Pump power
\( \dot{W}_{\text{PUMP}} \)

Ambient air
\( \dot{Q}_{\text{EVA}} \)

**Figure 2.4: Boundary of the double effect absorption system when it is used for heating.** The red dotted line displays the boundary of the system, the heat flows and power demand used to calculate the COP are displayed for the different components.

Pressure generator and goes to the first solution heat exchanger. The balances for the high pressure generator are as follows:

\[ \dot{m}_7 + \dot{m}_{11b} = \dot{m}_{11a} + \dot{m}_8 \]  
(2.5)

\[ x_7 \dot{m}_7 + x_{11b} \dot{m}_{11b} = y_{11a} \dot{m}_{11a} + x_8 \dot{m}_8 \]  
(2.6)

\[ \dot{Q}_{\text{HPG}} = \dot{m}_{11a} h_{11a} + \dot{m}_8 h_8 - \dot{m}_7 h_7 - \dot{m}_{11b} h_{11b} \]  
(2.7)

The vapor coming from the high pressure generator is cooled down in the rectifier to increase the quality of the vapor. The balances are as follows:

\[ \dot{m}_{11a} = \dot{m}_{11b} + \dot{m}_{11} \]  
(2.8)

\[ y_{11a} \dot{m}_{11a} = x_{11b} \dot{m}_{11b} + y_{11} \dot{m}_{11} \]  
(2.9)

\[ \dot{Q}_{\text{REC1}} = \dot{m}_{11a} h_{11a} - \dot{m}_{11b} h_{11b} - \dot{m}_{11} h_{11} \]  
(2.10)

A physical interpretation of the high pressure generator and rectifier is shown in figure 2.5. For working pairs with an absorbent with non-negligible vapor pressure, like ammonia-water, this purification section is needed. Stream 11a and stream 7 are in equilibrium. Furthermore, the following assumptions apply:

\[ T_{11} = T_{12} + 30K \]  
(2.11)

\[ T_{11b} = T_{11} - 20K \]  
(2.12)

The reflux ratio is calculated as follows:

\[ RR_{\text{REC1}} = \frac{m_{11b}}{m_{11}} = \frac{y_{11a} - y_{11}}{x_{11b} - y_{11a}} \]  
(2.13)
Intermediate pressure generator, high pressure condenser and the second rectifier  Saturated vapor from the high pressure generator (stream 11) is condensed in the high pressure condenser and the heat that is rejected ($Q_{HPC}$) is used to evaporate more ammonia coming from the first heat exchanger (stream 10). The intermediate pressure generator has a similar construction as the high pressure generator; the ammonia vapor goes to the rectifier where it is purified. The balances are as follows:

$$\dot{Q}_{REC} = \dot{m}_{14a} h_{14a} - \dot{m}_{14b} h_{14b} - \dot{m}_{14} h_{14}$$  \hspace{1cm} (2.14)$$

$$\dot{Q}_{HPC} = \dot{m}_{11} h_{11} - \dot{m}_{12} h_{12}$$  \hspace{1cm} (2.15)$$

$$\dot{Q}_{IPG} = \dot{m}_{15} h_{15} + \dot{m}_{14a} h_{14a} - \dot{m}_{10} h_{10} - \dot{m}_{14b} h_{14b}$$  \hspace{1cm} (2.16)$$

Where the following energy balance should hold:

$$\dot{m}_{10} h_{10} + \dot{m}_{11} h_{11} + \dot{m}_{14b} h_{14b} = \dot{m}_{15} h_{15} + \dot{m}_{12} h_{12} + \dot{m}_{14a} h_{14a}$$  \hspace{1cm} (2.17)$$

Or:

$$\dot{Q}_{HPC} = \dot{Q}_{IPG}$$  \hspace{1cm} (2.18)$$

For the second rectifier the mass balances are as follows:

$$\dot{m}_{14a} = \dot{m}_{14b} + \dot{m}_{14}$$  \hspace{1cm} (2.19)$$

$$y_{14a} \dot{m}_{14a} = x_{14b} \dot{m}_{14b} + y_{14} \dot{m}_{14}$$  \hspace{1cm} (2.20)$$

Furthermore, the following assumptions apply:

$$T_{14} = T_{1} + 30 K$$  \hspace{1cm} (2.21)$$

$$T_{14b} = T_{14} - 20 K$$  \hspace{1cm} (2.22)$$
2.2. Thermodynamic model

The reflux ratio can be calculated with:

\[
RR_{REC2} = \frac{m_{14b}}{m_{14}} = \frac{y_{14a} - y_{14}}{x_{14b} - y_{14a}} \tag{2.23}
\]

To determine the temperature at the solution outlet of the intermediate pressure generator a pinch temperature is assumed. This gives us the following relation:

\[
T_{15} = T_{12} + 5K \tag{2.24}
\]

**Condenser**  In the condenser heat is exchanged and a saturated liquid leaves the condenser. The balances for the condenser are:

\[
\dot{m}_{14} + \dot{m}_{13} = \dot{m}_{1} \tag{2.25}
\]

\[
y_{14} \dot{m}_{14} + y_{13} \dot{m}_{13} = x_{1} \dot{m}_{1} \tag{2.26}
\]

\[
\dot{Q}_{CON} = \dot{m}_{14} h_{14} + \dot{m}_{13} h_{13} - \dot{m}_{1} h_{1} \tag{2.27}
\]

**Absorber**  In the absorber, the solution coming from the intermediate pressure generator (stream 17) absorbs the vapor coming from the evaporator (stream 3). The rich solution leaves the absorber (stream 4) and gets pumped to the high pressure generator. During this process the absorber exchanges heat with the environment (\(\dot{Q}_{ABS}\)). The balances for the absorber are:

\[
\dot{m}_{3} + \dot{m}_{17} = \dot{m}_{4} \tag{2.28}
\]

\[
y_{3} \dot{m}_{3} + x_{17} \dot{m}_{17} = x_{4} \dot{m}_{4} \tag{2.29}
\]

\[
\dot{Q}_{ABS} = \dot{m}_{3} h_{3} + \dot{m}_{17} h_{17} - \dot{m}_{4} h_{4} \tag{2.30}
\]

**Evaporator**  The evaporator exchanges heat with the environment (\(\dot{Q}_{EVA}\)) while evaporating the ammonia flow. The ammonia leaves the evaporator as a saturated vapor (stream 3). The balances for the evaporator are:

\[
\dot{m}_{2} = \dot{m}_{3} \tag{2.31}
\]

\[
x_{2} \dot{m}_{2} = x_{2} \dot{m}_{3} \tag{2.32}
\]

\[
\dot{Q}_{EVA} = \dot{m}_{3} h_{3} - \dot{m}_{2} h_{2} \tag{2.33}
\]

**Heat exchangers (HEX1 and HEX2)**  To reduce the required heat input, two solution heat exchangers are used. Both heat exchangers are modelled using a pinch temperature of 5 K. The solution flows and their temperatures are illustrated in figure 2.6 and 2.7. Heat exchanger 1 uses the following balances:

\[
\dot{m}_{6}(h_{7} - h_{6}) = \dot{m}_{8}(h_{8} - h_{9}) \tag{2.34}
\]

\[
T_{9} = T_{6} + 5K \tag{2.35}
\]

The balance and assumption for heat exchanger 2 are as follows:

\[
\dot{m}_{5}(h_{6} - h_{5}) = \dot{m}_{15}(h_{15} - h_{16}) \tag{2.36}
\]

\[
T_{16} = T_{5} + 5K \tag{2.37}
\]
Valves All the valves are modelled isenthalpic which gives the following balances:

\[ h_{16} = h_{17} \]  
(2.38)  
\[ h_9 = h_{10} \]  
(2.39)  
\[ h_{12} = h_{13} \]  
(2.40)  
\[ h_1 = h_2 \]  
(2.41)

Now that \( Q_{EVA}, Q_{CON}, Q_{ABS} \) and \( Q_{HPG} \) are calculated, \( COP_{heating} \) and \( COP_{cooling} \) can be calculated using equation 2.1 and 2.2. The main calculation procedure is illustrated in figure 2.8. It makes use of three iterative loops. Firstly, the minimum concentration of the refrigerant flows is assumed \((y_{11} \text{ and } y_{14})\). For some operating conditions and design parameters, the vapor leaving one of the rectifiers can have a higher temperature than the vapor entering the rectifier which results in a negative reflux flow. In order to prevent this, the minimum purity of the refrigerant flows will be increased. For the last iteration loop \( T_{12} \) will be increased until equation 2.17 is satisfied. All the equations and iterative loops are implemented in the software package MATLAB [20].
Figure 2.8: Main calculation procedure for the double-effect absorption system in a series configuration. There are three iteration loops. Once the balance between the high pressure condenser and the intermediate pressure generator is satisfied the loop finishes.
2.3. Results and discussion

2.3.1. Cycle performance

This section discusses the behaviour and performance of the developed thermodynamic model. The operating conditions and design parameters are listed in table 2.1. These conditions have a strong impact on the performance. For the discussed case, the cycle uses waste heat at a temperature of 130 °C and it will supply the cooling demand at 0 °C. The absorber, the condenser and the rectifiers exchange heat with the environment at a temperature of 30 °C. The load of each component and the coefficient of performance of the absorption cycle under these conditions are shown in table 2.2. The performance of this cycle under these conditions is lower than the lithium-bromide and water double effect absorption system. However, this cycle does perform better than the single-effect absorption cycle using ammonia-water. All the properties at the state points are listed in table 2.3. As can be seen in table 2.2, the required pump power has a small effect on the performance.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{CON}}$</td>
<td>30</td>
<td>[°C]</td>
<td>Condensation temperature</td>
</tr>
<tr>
<td>$T_{\text{ABS}}$</td>
<td>30</td>
<td>[°C]</td>
<td>Temperature of the absorber solution outlet</td>
</tr>
<tr>
<td>$T_{\text{HPG}}$</td>
<td>130</td>
<td>[°C]</td>
<td>High pressure generator solution outlet temperature</td>
</tr>
<tr>
<td>$T_{\text{EVA}}$</td>
<td>0</td>
<td>[°C]</td>
<td>Evaporation temperature</td>
</tr>
<tr>
<td>$dT_{\text{IPG}}$</td>
<td>5</td>
<td>[K]</td>
<td>Pinch temperature in the intermediate pressure generator</td>
</tr>
<tr>
<td>$dT_{\text{HEX}_1}$</td>
<td>5</td>
<td>[K]</td>
<td>Pinch temperature in the first heat exchanger</td>
</tr>
<tr>
<td>$dT_{\text{HEX}_2}$</td>
<td>5</td>
<td>[K]</td>
<td>Pinch temperature in the second heat exchanger</td>
</tr>
<tr>
<td>$\eta_{\text{PUMP}}$</td>
<td>0.9</td>
<td>[-]</td>
<td>Pump efficiency</td>
</tr>
<tr>
<td>$y_{\text{NH}_3}$</td>
<td>0.999</td>
<td>[-]</td>
<td>Purity of ammonia in the refrigerant cycle</td>
</tr>
<tr>
<td>$\dot{m}_{5}$</td>
<td>1</td>
<td>[kg/s]</td>
<td>Mass flow through the pump</td>
</tr>
<tr>
<td>$dT_{11}$</td>
<td>30</td>
<td>[K]</td>
<td>Temperature difference between $T_{11}$ and $T_{12}$</td>
</tr>
<tr>
<td>$dT_{11b}$</td>
<td>10</td>
<td>[K]</td>
<td>Temperature difference between $T_{11b}$ and $T_{12}$</td>
</tr>
<tr>
<td>$dT_{14}$</td>
<td>30</td>
<td>[K]</td>
<td>Temperature difference between $T_{14}$ and $T_{1}$</td>
</tr>
<tr>
<td>$dT_{14b}$</td>
<td>10</td>
<td>[K]</td>
<td>Temperature difference between $T_{14b}$ and $T_{1}$</td>
</tr>
</tbody>
</table>

Table 2.1: Operating conditions and design parameters for the double-effect absorption cycle during cooling. All input parameters for the mathematical model. Their influence on the performance of the cycle is investigated in chapter 2.3.3.
2.3. Results and discussion

Table 2.2: Results obtained from the model. The results for the mathematical model for the conditions: $T_{\text{ABS}} = T_{\text{CON}} = 30 \, ^\circ\text{C}$, $T_{\text{EVA}} = 0 \, ^\circ\text{C}$ and $T_{\text{HPG}} = 130 \, ^\circ\text{C}$. All other the input values for these results are listed in table 2.1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{Q}_{\text{EVA}}$</td>
<td>102.39</td>
<td>[kW]</td>
<td>Heat flow in the evaporator</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{ABS}}$</td>
<td>146.84</td>
<td>[kW]</td>
<td>Heat flow in the absorber</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{COND}}$</td>
<td>52.136</td>
<td>[kW]</td>
<td>Heat flow in the condenser</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{HPG}}$</td>
<td>118.63</td>
<td>[kW]</td>
<td>Heat added to the High pressure generator</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{IPG}}$</td>
<td>56.730</td>
<td>[kW]</td>
<td>Heat exchanged in the intermediate pressure generator</td>
</tr>
<tr>
<td>$W_{\text{PUMP}}$</td>
<td>4.6977</td>
<td>[kW]</td>
<td>Pump power</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{REC1}}$</td>
<td>23.032</td>
<td>[kW]</td>
<td>Heat rejected in the first rectifier</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{REC2}}$</td>
<td>3.2856</td>
<td>[kW]</td>
<td>Heat rejected in the second rectifier</td>
</tr>
<tr>
<td>$\text{COP}_{\text{cooling}}$</td>
<td>0.83022</td>
<td>[-]</td>
<td>COP for cooling</td>
</tr>
<tr>
<td>$R_{\text{REC1}}$</td>
<td>0.3002</td>
<td>[-]</td>
<td>Reflux ratio in the first rectifier</td>
</tr>
<tr>
<td>$R_{\text{REC2}}$</td>
<td>0.0505</td>
<td>[-]</td>
<td>Reflux ratio in the second rectifier</td>
</tr>
</tbody>
</table>

2.3.2. Influence of the operating conditions on the performance

In order to find the most suitable application for this absorption cycle using ammonia and water, it is useful to look at the influence of the operating condition on the performance. Figure 2.9 shows the COP for different evaporator outlet temperatures while varying the outlet temperature of the high pressure generator. There is a minimum $T_{\text{HPG}}$ for every evaporator temperature. To explain this minimum, we have to take a closer look at the high pressure generator. At point 7 we have the strong solution at the inlet of the high pressure generator from which ammonia will be desorbed. The concentration of stream 7 is the same as the stream leaving the absorber (stream 4) which is determined by $P_{\text{EVA}}$ and $T_{\text{ABS}}$. By increasing $T_{\text{EVA}}$, the evaporator pressure $P_{\text{EVA}}$ also increases. The ammonia concentration of the solution increases with increasing pressure so the concentration of the high pressure generator inlet becomes higher with increasing evaporator outlet temperature. When the concentration of the high pressure generator inlet is higher, more ammonia can be evaporated which explains the higher COP for higher evaporator temperatures. Of course the concentration of the solution leaving the high pressure generator has to be lower than the concentration of the inlet. So if $T_{\text{HPG}}$ becomes too low, the concentration of the outlet will become higher than the concentration of the inlet causing the system to fail which explains the minimum $T_{\text{HPG}}$. For lower evaporation temperatures it is beneficial to have higher $T_{\text{HPG}}$ because this results in a higher COP. Because this model assumes equilibrium conditions at stream 11a, the temperature at this point cannot be higher than the critical temperature which is dependent on the composition of the solution. When increasing $T_{\text{HPG}}$, the ammonia concentration of stream 11a decreases so the critical temperature increases. Unfortunately, the temperature of the stream increases faster than the critical temperature with increasing $T_{\text{HPG}}$ so a maximum will be reached.

Figure 2.10 shows the COP of the absorption cycle for different absorber and condenser outlet temperatures. The performance of the cycle is significantly lower for higher absorber and condenser outlet temperatures. Additionally, the operating range is a lot smaller for higher absorber and condenser outlet temperatures. When the condenser outlet temperature increases, the intermediate pressure $P_{\text{CON}}$ also increases. This increases the lowest solution concentration level ($x_{15}$) which has to be lower than the absorber outlet concentration ($x_4$). In turn, when increasing $T_{\text{HPG}}$ the lowest solution concentration level goes up. This means that for higher absorber and condenser outlet temperatures there is a higher minimum $T_{\text{HPG}}$. 
2. Double-Effect absorption system with ammonia-water

**Figure 2.9:** The COP of the double effect absorption cycle as a function of the outlet solution temperature of the high pressure generator for different evaporator temperatures. The COP is displayed for different evaporation temperatures. The absorber and condenser temperature are kept constant at 30 °C, all other parameters are listed in table 2.1.

**Figure 2.10:** The COP of the double effect absorption cycle as a function of the outlet solution temperature of the high pressure generator for different absorber and condenser temperatures. The COP is displayed for different absorber and condenser temperatures. The evaporation temperature is kept constant at 0 °C, all other parameters are listed in table 2.1.
Table 2.3: State properties of the double effect absorption cycle during cooling. for the conditions: \( T_{\text{ABS}} = T_{\text{CON}} = 30 \) °C, \( T_{\text{EVA}} = 0 \) °C and \( T_{\text{HPG}} = 130 \) °C. All other operating parameters are listed in table 2.1. The heat flows and reflux ratios are displayed in table 2.2.

<table>
<thead>
<tr>
<th>Massflow [kg/s]</th>
<th>Temperature [°C]</th>
<th>Concentration</th>
<th>Pressure [bar]</th>
<th>Enthalpy [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.087</td>
<td>30.000</td>
<td>0.999</td>
<td>11.670</td>
</tr>
<tr>
<td>2</td>
<td>0.087</td>
<td>0.031</td>
<td>0.999</td>
<td>4.294</td>
</tr>
<tr>
<td>3</td>
<td>0.087</td>
<td>0.000</td>
<td>0.999</td>
<td>4.294</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>30.000</td>
<td>0.510</td>
<td>4.294</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>30.305</td>
<td>0.510</td>
<td>39.471</td>
</tr>
<tr>
<td>6</td>
<td>1.000</td>
<td>64.320</td>
<td>0.510</td>
<td>39.471</td>
</tr>
<tr>
<td>7</td>
<td>1.000</td>
<td>121.519</td>
<td>0.510</td>
<td>39.471</td>
</tr>
<tr>
<td>8</td>
<td>0.944</td>
<td>130.000</td>
<td>0.481</td>
<td>39.471</td>
</tr>
<tr>
<td>9</td>
<td>0.944</td>
<td>69.320</td>
<td>0.481</td>
<td>39.471</td>
</tr>
<tr>
<td>10</td>
<td>0.944</td>
<td>69.678</td>
<td>0.481</td>
<td>11.670</td>
</tr>
<tr>
<td>11</td>
<td>0.056</td>
<td>107.792</td>
<td>0.999</td>
<td>39.471</td>
</tr>
<tr>
<td>11a</td>
<td>0.073</td>
<td>121.519</td>
<td>0.966</td>
<td>39.471</td>
</tr>
<tr>
<td>11b</td>
<td>0.017</td>
<td>87.792</td>
<td>0.858</td>
<td>39.471</td>
</tr>
<tr>
<td>12</td>
<td>0.056</td>
<td>77.791</td>
<td>0.999</td>
<td>39.471</td>
</tr>
<tr>
<td>13</td>
<td>0.056</td>
<td>30.047</td>
<td>0.999</td>
<td>11.670</td>
</tr>
<tr>
<td>14</td>
<td>0.031</td>
<td>60.000</td>
<td>0.999</td>
<td>11.670</td>
</tr>
<tr>
<td>14a</td>
<td>0.033</td>
<td>69.678</td>
<td>0.989</td>
<td>11.670</td>
</tr>
<tr>
<td>14b</td>
<td>0.002</td>
<td>40.000</td>
<td>0.785</td>
<td>11.670</td>
</tr>
<tr>
<td>15</td>
<td>0.913</td>
<td>72.792</td>
<td>0.463</td>
<td>11.670</td>
</tr>
<tr>
<td>16</td>
<td>0.913</td>
<td>35.305</td>
<td>0.463</td>
<td>11.670</td>
</tr>
<tr>
<td>17</td>
<td>0.913</td>
<td>35.413</td>
<td>0.463</td>
<td>4.294</td>
</tr>
</tbody>
</table>

Figure 2.11 shows the reflux ratio for the high pressure generator at different \( T_{\text{HPG}} \). When \( T_{\text{HPG}} \) increases, the inlet temperature (stream 7) of the high pressure generator also increases because they exchange heat in HEX1. Stream 7 and stream 11a are assumed to be in equilibrium, so \( T_{11a} \) increases with increasing \( T_{\text{HPG}} \) giving the stream a lower concentration. When stream 11a has a lower concentration, more water has to be removed from this stream in the rectifier, resulting in a higher reflux ratio.

Figure 2.12 shows the heat flow in the high pressure generator and the evaporator with varying \( T_{\text{HPG}} \). With increasing \( T_{\text{HPG}} \) both heat flows increase, however, the high pressure generator input heat increases with a higher rate. This means that there is an optimum COP and it will decrease for higher temperatures. When the temperature increases, there is more water content in the vapor leaving the high pressure generator. This extra water content does not contribute to the cooling power, but it does need more heat input to evaporate.

Figure 2.13 shows the amount of heat that has to be extracted in the rectifiers to condense the water content in the vapor. The rejected heat in the first rectifier is strongly dependent on the high pressure generator solution outlet temperature. This explains why the high pressure generator input heat increases faster than the cooling power, and thus why the COP decreases with increasing \( T_{\text{HPG}} \).
2. Double-Effect absorption system with ammonia-water

Figure 2.11: The reflux ratio of the rectifier of the high pressure generator for different absorber and condenser properties. For the conditions: \( T_{ABS} = T_{CON} = 30 \, ^\circ C \) and \( T_{EVA} = 0 \, ^\circ C \). The reflux ratio is calculated with equation 2.13. The high pressure generator reflux ratio shows a stronger increase because it is directly connected to the high pressure generator.

2.3.3. Influence of the design parameters on the performance

Figure 2.14 shows the COP as a function of the ammonia purity in the refrigerant stream. From the figure it can be seen that the COP decreases with increasing purity. This is because more heat has to be removed from the stream to condense the water. This heat has to be added in the high pressure generator resulting in a lower COP.

Figure 2.15 shows the COP of the cycle as a function of the superheating temperature of the vapor stream leaving the rectifiers. This is the temperature difference between \( T_{12} \) and \( T_{11} \) and \( T_{1} \) and \( T_{14} \). In this model, a superheating temperature of 30 K is assumed. Increasing the superheating temperature of stream 11 results in a higher COP for cooling applications. When the superheating temperature increases, more heat is rejected in the high pressure condenser and released to the intermediate pressure generator, which in turn, has more heat to generate more ammonia. However, increasing the superheating temperature in the second rectifier \((dT_{14})\) has no effect on the COP for a cooling application. A higher superheating temperature does result in a higher enthalpy at point 14, but this extra energy is rejected to the environment in the second rectifier and the condenser, which does not have an effect on the COP.

Figure 2.16 shows the temperature difference between the temperature of the superheated vapor and the temperature of the liquid reflux stream leaving the rectifiers. The COP for a cooling application increases when increasing \( dT_{14b} \) and \( dT_{11b} \).
2.3. Results and discussion

Figure 2.12: The heat flow in the high pressure generator and the evaporator. For the operating conditions: $T_{ABS} = T_{CON} = 30 \degree C$ and $T_{EVA} = 0 \degree C$. The high pressure generator heat flows shows a stronger increase resulting in a lower COP for higher $T_{HPG}$.

Figure 2.13: The heat flow in the rectifiers. For the operating conditions: $T_{ABS} = T_{CON} = 30 \degree C$ and $T_{EVA} = 0 \degree C$. The first rectifier shows a much stronger increase because it is directly connected to the high pressure generator. When the high pressure generator operates at higher temperatures, more water has to be condensed from the vapor stream.
For the conditions: $T_{\text{ABS}} = T_{\text{CON}} = 30 \, ^\circ\text{C}$, $T_{\text{EVA}} = 0 \, ^\circ\text{C}$ and $T_{\text{HPG}} = 130 \, ^\circ\text{C}$. All other operating conditions and design parameters are listed in table 2.1. A strong decrease in COP for higher purities can be seen because more heat is rejected to the environment in the rectifiers.

2.4. Conclusions

In this chapter, the mathematical modelling of the double-effect ammonia water absorption cycle has been described in detail. The purpose of the model is to investigate the suitability of the ammonia water working pair in this cycle for cooling or heating applications. Additionally, the model can be used to investigate the effect of different operating conditions and design parameters on the performance. The mass and energy balances of all the individual components are implemented and solved using the software package Matlab, where the properties of the ammonia and water mixture are taken from NIST’s REFPROP database. Based on the findings of this model, the following conclusions are drawn:

- For temperatures above 0 °C, lithium bromide as working pair for this cycle has the preference because the performance is significantly better.
- The necessity of rectification has a negative effect on the performance.
- For high absorber and condenser outlet temperatures the cycle has a very small operating range so the cycle is not suitable for heating applications.
- The pump power has a small effect on the performance of the cycle.
2.4. Conclusions

Figure 2.15: The COP of the double effect absorption cycle as a function of the superheating temperature of the vapor leaving the high pressure generator. For the conditions $T_{ABS} = T_{CON} = 30 \, ^\circ C$, $T_{EVA} = 0 \, ^\circ C$ and $T_{HPG} = 130 \, ^\circ C$. All other operating conditions and design parameters are listed in table 2.1.

Figure 2.16: The COP of the double effect absorption cycle as a function of the temperature difference of the liquid reflux streams leaving the rectifiers. For the conditions $T_{ABS} = T_{CON} = 30 \, ^\circ C$, $T_{EVA} = 0 \, ^\circ C$ and $T_{HPG} = 130 \, ^\circ C$. All other operating conditions and design parameters are listed in table 2.1.
Double-effect absorption cycle with ammonia-ionic liquid working pairs

3.1. Introduction

This chapter describes a method to determine vapor-liquid equilibrium and enthalpy properties for nine ionic liquid and ammonia working pairs from experimental data. The properties are used to predict the performance of the nine working pairs in a double-effect absorption cycle. A method to predict the suitability of the working pairs without doing any cycle calculations is presented and the influence of the design parameters and the operating conditions on the performance is discussed.

3.2. Properties

Vapor-liquid equilibrium and enthalpy are two of the fundamental properties to calculate the performance of working pairs for absorption cycles. They describe the relationship between the pressure, temperature and composition and those with the enthalpy respectively. Equations 3.1-3.6 describe a non-random two-liquid (NRTL) model to predict the vapor liquid equilibrium of mixtures. Due to the non-volatility of ionic liquids, its fraction in the vapor phase can be neglected. In that case, the equilibrium criterion can be simplified to equation 3.1 where $P_{\text{sat}}^{NH_3}$ can be obtained from NIST’s Refprop [17]. With experimental vapor liquid equilibrium data the binary parameters $\alpha$, $\tau_{12}^{(0)}$, $\tau_{12}^{(1)}$, $\tau_{21}^{(0)}$ and $\tau_{21}^{(1)}$ in the NRTL model are correlated and will allow for the determination of the operating concentrations. The correlated parameters are listed in table 3.1. Eight of the nine working pairs have been correlated with a Root-mean-square deviation (RMSD) smaller than 5.6 %. Only the model for the working pair ammonia and [Omim][BF4] showed a slightly larger deviation of 8.7 %. The equations are implemented in the software package Matlab by Wang and Ferreira [33].

$$
\gamma_{NH_3} = \frac{P}{x_{NH_3}P_{\text{sat}}^{NH_3}}
$$

(3.1)

The activity coefficient $\gamma_{NH_3}$ needed for equation 3.1 can be obtained by the NRTL activity coefficient model:

$$
\ln(\gamma_i) = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right]
$$

(3.2)
Where the NRTL parameters can be calculated with equation 3.3-3.6.

\[ G_{12} = \exp(-\alpha \tau_{12}) \] (3.3)
\[ G_{21} = \exp(-\alpha \tau_{21}) \] (3.4)
\[ \tau_{12} = \tau_{12}^{(0)} + \frac{\tau_{12}^{(1)}}{T} \] (3.5)
\[ \tau_{21} = \tau_{21}^{(0)} + \frac{\tau_{21}^{(1)}}{T} \] (3.6)

The enthalpy data for pure ammonia is directly obtained from NIST’s REFPROP [17]. For a real solution the total enthalpy can be calculated as the sum of the enthalpy for the ideal solution and the mixing heat, which is expressed by equation 3.7.

\[ h = x_{NH_3} h_{NH_3} + x_{IL} h_{IL} + h_{mix} \] (3.7)

In this work, the mixing heat part \( h_{mix} \), is neglected. This means that the equation simplifies to:

\[ h = x_{NH_3} h_{NH_3} + x_{IL} h_{IL} \] (3.8)

The enthalpy of the pure ionic liquid can be obtained from the heat capacity of the pure ionic liquid according to equation 3.9.

\[ h_{IL} = h_0 + \int_{T_0}^{T} c_{pIL} dT \] (3.9)

Where the heat capacity can be expressed by the linear equation 3.10, using the correlated parameters listed in table 3.2. Furthermore, to prevent the ionic liquids from chemically decomposing, the cycle should operate below the decomposition temperatures. For eight of the nine ionic liquids the decomposition is known from experimental data, they are listed in table 3.3. The ionic liquid \([Emim][SCN] \) has the lowest decomposition temperature of 250 °C, which is below conventional operating temperatures of the double-effect absorption cycle.

\[ c_{p} = c_0 + c_1 T \] (3.10)

Table 3.1: Correlated binary parameters in the NRTL model. The NRTL parameters are correlated using experimental data of vapor-liquid equilibrium measurements. The maximum RMSD is 8.71% [33].

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>( \alpha )</th>
<th>( \tau_{12}^{(0)} )</th>
<th>( \tau_{12}^{(1)} )</th>
<th>( \tau_{21}^{(0)} )</th>
<th>( \tau_{21}^{(1)} )</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bmim][BF4]</td>
<td>-0.01296</td>
<td>-48.0115</td>
<td>8926.476</td>
<td>32.42976</td>
<td>-5461.79</td>
<td>Yokozeki and Shiflett [37]</td>
</tr>
<tr>
<td>[Bmim][PF6]</td>
<td>0.334114</td>
<td>3.729984</td>
<td>-509.569</td>
<td>-4.18755</td>
<td>643.4984</td>
<td>Yokozeki and Shiflett [37]</td>
</tr>
<tr>
<td>[Emim][BF4]</td>
<td>0.999524</td>
<td>-0.00571</td>
<td>236.4087</td>
<td>-1.25914</td>
<td>164.5906</td>
<td>Li et al. [18]</td>
</tr>
<tr>
<td>[Emim][PF6]</td>
<td>0.716041</td>
<td>11.16699</td>
<td>-4089.25</td>
<td>-7.52981</td>
<td>2451.455</td>
<td>Yokozeki and Shiflett [36]</td>
</tr>
<tr>
<td>[Emim][SCN]</td>
<td>-0.00422</td>
<td>-99.9992</td>
<td>14710.17</td>
<td>71.51013</td>
<td>-9046.21</td>
<td>Yokozeki and Shiflett [37]</td>
</tr>
<tr>
<td>[Emim][TF2N]</td>
<td>0.999976</td>
<td>-14.8044</td>
<td>5081.738</td>
<td>-2.66902</td>
<td>478.851</td>
<td>Li et al. [18]</td>
</tr>
<tr>
<td>[Emim][DMP]</td>
<td>0.240323</td>
<td>7.819133</td>
<td>-2300.68</td>
<td>-4.42766</td>
<td>1000.393</td>
<td>Sun et al. [31]</td>
</tr>
<tr>
<td>[Oimim][BF4]</td>
<td>0.907017</td>
<td>-7.01386</td>
<td>2690.743</td>
<td>-2.39948</td>
<td>283.1702</td>
<td>Li et al. [18]</td>
</tr>
</tbody>
</table>
Table 3.2: Correlated parameters. In the equation $c_p = c_0 + c_1 T$ for mole-based $c_p$. The maximum RMSD is 0.94% [33]

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>$c_0$</th>
<th>$c_1$</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bmim][BF4]</td>
<td>250.2006</td>
<td>0.39721</td>
<td>Paulechka et al. [25]</td>
</tr>
<tr>
<td>[Bmim][PF6]</td>
<td>282.0703</td>
<td>0.452468</td>
<td>Kabo et al. [14]</td>
</tr>
<tr>
<td>[Emim][BF4]</td>
<td>214.0669</td>
<td>0.307615</td>
<td>Yu et al. [38]</td>
</tr>
<tr>
<td>[Emim][EtOSO3]</td>
<td>245.5262</td>
<td>0.461986</td>
<td>Paulechka et al. [25]</td>
</tr>
<tr>
<td>[Emim][SCN]</td>
<td>116.4736</td>
<td>0.546945</td>
<td>Navarro et al. [21]</td>
</tr>
<tr>
<td>[Emim][Tf2N]</td>
<td>363.1883</td>
<td>0.478096</td>
<td>Paulechka et al. [24]</td>
</tr>
<tr>
<td>[Hmim][BF4]</td>
<td>275.962</td>
<td>0.52</td>
<td>Waliszewski [32]</td>
</tr>
<tr>
<td>[Mmim][DMP]</td>
<td>-153.898</td>
<td>1.476179</td>
<td>He et al. [12]</td>
</tr>
<tr>
<td>[Omim][BF4]</td>
<td>323.8942</td>
<td>0.587683</td>
<td>Paulechka et al. [25]</td>
</tr>
</tbody>
</table>

Table 3.3: Decomposition temperatures. The temperature at which the ionic liquids start to chemically decompose, the operating temperature range of the investigated absorption cycle is below this limit.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>$T_{dec}$ [°C]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Emim][EtOSO3]</td>
<td>&gt;330</td>
<td>Wasserscheid and Welton [34]</td>
</tr>
<tr>
<td>[Emim][SCN]</td>
<td>&gt;250</td>
<td>Navarro et al. [21]</td>
</tr>
<tr>
<td>[Emim][Tf2N]</td>
<td>&gt;330</td>
<td>Chen et al. [7]</td>
</tr>
<tr>
<td>[Hmim][BF4]</td>
<td>&gt;332</td>
<td>Cao and Mu [5]</td>
</tr>
</tbody>
</table>

3.3. Thermodynamic model

A simplified process flow diagram of the double effect absorption cycle in series configuration is shown in figure 3.1. This model is similar to the model for the ammonia water working pair from chapter 2. However, as the ionic liquids are assumed to be non-volatile, there is no need for rectifiers. Without rectifiers, the energy balances for the high pressure generator, the absorber, the condenser, the evaporator and the intermediate pressure generator are given by equation 3.11-3.15. Furthermore, the refrigerant flow is modeled as pure ammonia and the design parameters are listed in table 3.4. The main calculation procedure is illustrated in figure 3.2.

$$
\dot{Q}_{HPG} = \dot{m}_8 h_8 + \dot{m}_{11} h_{11} - \dot{m}_7 h_7
$$

$$
\dot{Q}_{ABS} = \dot{m}_{17} h_{17} + \dot{m}_3 h_3 - \dot{m}_4 h_4
$$

$$
\dot{Q}_{CON} = \dot{m}_{14} h_{14} + \dot{m}_{13} h_{13} - \dot{m}_1 h_1
$$

$$
\dot{Q}_{EVA} = \dot{m}_3 h_3 - \dot{m}_2 h_2
$$

$$
\dot{m}_{11} (h_{11} - h_{12}) = \dot{m}_{14} h_{14} + \dot{m}_{15} h_{15} - \dot{m}_{10} h_{10}
$$

To quantify the performance of the model, equations 3.16 and 3.17 are used to calculate the COP for cooling and heating applications respectively.

$$
COP_{cooling} = \frac{\dot{Q}_{EVA}}{\dot{Q}_{HPG}}
$$

$$
COP_{heating} = \frac{\dot{Q}_{ABS} + \dot{Q}_{CON}}{\dot{Q}_{HPG}}
$$
3. Double-effect absorption cycle with ammonia-ionic liquid working pairs

Figure 3.1: Process flow diagram of the double-effect absorption cycle in a series configuration. The red, blue, purple and green lines indicate the strong solution, the intermediate solution, the weak solution and the refrigerant flows, respectively. The dotted lines indicate the vapor phase and the solid lines indicate the liquid phase.

Figure 3.2: Main calculation procedure for the double-effect absorption system in a series configuration without rectifiers. In contrast to the calculation procedure using ammonia and water as working pair, there is only one iteration loop because there are no rectifiers in the cycle.
Table 3.4: Design parameters for the double-effect absorption cycle using ammonia and ionic liquids as working pair.
The mass flow through the pump can be adjusted to increase all the heat flows, and thus the heating or cooling demand. The influence of the design parameters is discussed later.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dT_{IPG}$</td>
<td>5</td>
<td>[K]</td>
<td>Pinch temperature in the IPG</td>
</tr>
<tr>
<td>$dT_{HEX1}$</td>
<td>5</td>
<td>[K]</td>
<td>Pinch temperature in HEX1</td>
</tr>
<tr>
<td>$dT_{HEX2}$</td>
<td>5</td>
<td>[K]</td>
<td>Pinch temperature in HEX2</td>
</tr>
<tr>
<td>$\eta_{PUMP}$</td>
<td>0.9</td>
<td>[-]</td>
<td>Pump efficiency</td>
</tr>
<tr>
<td>$\dot{m}_4$</td>
<td>1</td>
<td>[kg/s]</td>
<td>Mass flow through the pump</td>
</tr>
</tbody>
</table>

### 3.4. Results and discussion

#### 3.4.1. Thermodynamic restrictions

The range of working conditions for the working pairs can be determined without making any absorption cycle calculations. By using vapor liquid equilibrium data and restrictions of the thermodynamic model, the limits of the operating conditions can be determined. In the intermediate pressure generator and the high pressure generator, the concentration of the solution at the outlets (stream 8 and 15) should be smaller than at the inlets (stream 7 and stream 10). For the absorber the solution outlet concentration should be higher. So the restrictions for the absorber, high pressure generator and intermediate pressure generator are respectively:

\[
x_4 > x_{17}
\]

(3.18)

\[
(x_7 = x_4) > x_8
\]

(3.19)

\[
x_{10} > (x_{15} = x_{17})
\]

(3.20)

As explained in chapter 2, the thermodynamic model finds a $T_{12}$ for which the energy is balanced in the cycle, when equation 3.15 is satisfied. By using the restrictions and VLE-data, the range of $T_{12}$ can be determined. Every restriction gives a limit for $T_{12}$. To determine these limits, we take a closer look at the phase diagrams (figure 3.3- 3.5). The outlet of the evaporator is pure saturated ammonia vapor at a temperature $T_{EVA}$. This gives us the lowest pressure level $P_{EVA}$. From $P_{EVA}$ and $T_{ABS}$ the strongest solution concentration $x_4$ can be determined. The intermediate pressure level $P_{CON}$ is determined by $T_{CON}$. This means that the only parameters that are fixed by the operating conditions are $P_{EVA}$, $P_{CON}$ and $x_4$. All other parameters are directly or indirectly dependent on $T_{12}$.

**Restriction from the absorber**  The absorber operates at $P_{EVA}$, and the strong solution outlet has a temperature $T_{ABS}$ giving us the strong solution outlet concentration $x_4$, the blue line in figure 3.3. The concentration of the absorber solution inlet (stream 17) is determined at the outlet of the intermediate pressure generator (stream 15) which operates at $P_{CON}$ and $T_{15}$. The limit where the absorber can operate is at $x_4=x_{17}$. To determine the corresponding minimum temperature of this limit we have to solve:

\[
x_4(T_{ABS}, P_{EVA}) = x_{15}(T_{15}, P_{CON})
\]

(3.21)

By using the pinch temperature of the intermediate pressure generator ($T_{12}=T_{15}+5K$), a minimum temperature of $T_{12}$, shown in figure 3.3, can be found. When $T_{12}$ becomes lower than this value, $x_{15}$ becomes higher than $x_4$ causing the absorber to fail.
3. Double-effect absorption cycle with ammonia-ionic liquid working pairs

**Figure 3.3: ln(P) - 1/T phase diagram to find a minimum temperature for T12.** Resulting from the restriction of the absorber. The green and blue line indicate the pure ammonia line and the solution concentration line, respectively. Horizontal lines are isobars, vertical lines are isotherms and isoconcentration lines are diagonal.

**Restriction from the high pressure generator** To determine the upper limit of $T_{12}$ we take a look at the high pressure generator and equation 3.19. The limit where the high pressure generator can operate is at $x_4 = x_8$ (where $x_4 = x_7$). To find this limit we have to find a solution for equation 3.22.

$$x_4(T_{ABS}, P_{EVA}) = x_8(T_{HPG}, P_{PHG})$$

(3.22)

The process of finding this solution is illustrated in figure 3.4. The intersection of the constant concentration line (where $x_7 = x_8$) and $T_{HPG}$ results in the maximum $P_{HPG}$. The corresponding maximum limit of $T_{12}$ can be directly determined from $P_{HPG}$. $P_{HPG}$ is determined by the pure liquid refrigerant outlet of the intermediate pressure generator (stream 12). So we can get $T_{12\text{max}}$ from the pure ammonia line, as illustrated in figure 3.4. If $T_{12}$ becomes higher than this limit, $P_{HPG}$ will increase which in turn increases $x_8$ causing the high pressure generator to fail because $x_8$ becomes higher than $x_4$. 


3.4. Results and discussion

Restriction from the intermediate pressure generator  The third restriction, equation 3.20, will give another minimum limit for $T_{12}$. The weak solution outlet concentration of the intermediate pressure generator, $x_{15}$, is dependent on $P_{CON}$ and $T_{15}$. $P_{CON}$ is fixed by $T_{CON}$, and $x_{15}$ is determined by $T_{15}$, where $T_{15} = T_{12} - 5\,\text{K}$. The solution inlet concentration, $x_{10}$ (where $x_{10} = x_8$), is determined by $T_{HPG}$ and $P_{HPG}$. $P_{HPG}$ is determined by $T_{12}$, so both concentrations are dependent on $T_{12}$. The limit at which the IPG can operate is at $x_{10} = x_{15}$ (where $x_{10} = x_8$). The corresponding $T_{12}$ can be found by iteratively solving equation 3.23, a physical interpretation is illustrated in figure 3.5. Because $x_8$ increases with increasing $T_{12}$ and $x_{15}$ decreases with increasing $T_{12}$, $T_{12}$ should always be higher than the found limit.

$$x_8(T_{HPG}, P_{HPG}) = x_{15}(T_{15}, P_{CON})$$  \hspace{1cm} (3.23)

Before predicting the performance of the thermodynamic model, an analysis of the operating conditions is required. Tables 3.5 and 3.6 list the range of $T_{12}$ for 9 ammonia-ionic liquid working pairs for a cooling and heating application, respectively. In the tables, two minima and one maximum for $T_{12}$ are shown. To have a possible range for $T_{12}$, both minima must be lower than the maximum. Five of the nine working pairs cannot be operated at these conditions so limited or no possible working conditions are expected. The pairs with [Bmim][BF4], [Emim][BF4], [Emim][SCN] and [Mmim][DMP] show a small range of $T_{12}$ which suggests that there is an operating range, but it is very limited.

3.4.2. Performance prediction

The previous chapter made clear that some of the working pairs in this cycle are not very flexible. From tables 3.5 and 3.6 one would expect [Bmim][BF4], [Emim][BF4], [Emim][SCN] and [Mmim][DMP] to be most flexible and have the highest COP for the cycle. Figure 3.6 shows the $COP_{cooling}$ for the working pairs at $T_{ABS}=30\,\text{C}$, $T_{CON}=30\,\text{C}$, $T_{CON}$ and $T_{EVA}=10\,\text{C}$ for different $T_{HPG}$.
3. Double-effect absorption cycle with ammonia-ionic liquid working pairs

These operating conditions are not realistic but give an opportunity to compare most of the ionic liquids. Seven out of the nine working pairs can operate at these conditions. All four ionic liquids that had a possible range for the conditions in tables 3.5 and 3.6 have the highest COP. The ionic liquid with the largest range of possible $T_{12}$, [Mmim][DMP], has the highest COP for most of the range. For two ionic liquids, [Hmim][BF4] and [Emim][EtOSO3] no $T_{12}$ could be found to satisfy the energy balance, so they are not displayed in figure 3.6. The ILs [Bmim][PF6] and [Omim][BF4], which didn’t show promise, did give a result, but they have a lower COP than the other four ILs. These results show that having a large range for $T_{12}$ could be an indicator of better performance.

3.4.3. Performance prediction for cooling applications

The four best working pairs are selected for further investigation. For the operating conditions listed in table 3.5, the performance of the four working pairs is displayed in figure 3.7. As expected from the investigation of the range of $T_{12}$ in table 3.5, [Mmim][DMP] has the largest operating range followed by [Bmim][BF4]. Out of the investigated ionic liquids, [Bmim][BF4] reaches the highest COP so its performance will be described in detail. In further investigations the COP and the pump power are calculated with equations 3.24-3.26. The densities used to calculate the pump power for the investigated absorber temperature range are listed in table 3.7.

\[
COP_{cooling} = \frac{\dot{Q}_{EVA}}{\dot{Q}_{HPG} + \dot{W}_{PUMP}} \tag{3.24}
\]

\[
\dot{W}_{pump} = \frac{m_4}{\rho_{sol}} \frac{(P_{HPG} - P_{EVA})}{\eta_{PUMP}} \tag{3.25}
\]

\[
\rho_{sol} = x_4 \rho_{NH_3} + (1 - x_4) \rho_{IL} \tag{3.26}
\]
Figure 3.6: The COP of the double effect absorption cycle as a function of the driving temperature. For the conditions: $T_{ABS} = T_{CON} = 30\, ^\circ C$ and $T_{EVA} = 10\, ^\circ C$ using seven of the nine investigated ionic liquids. For the absorbents $[\text{Emim}]\text{EtOSO}_3$ and $[\text{Hmim}]\text{BF}_4$ no operating temperature could be found that did not violate a restriction.

Figure 3.7: The COP of the double effect absorption cycle as a function of the driving temperature. For the conditions: $T_{ABS} = T_{CON} = 40\, ^\circ C$ and $T_{EVA} = 5\, ^\circ C$ using the four best performing ionic liquids as absorbent. The ionic liquid $[\text{Bmim}]\text{BF}_4$ shows the best performance for most of the investigated temperature range.
Table 3.5: Range of \( T_{12} \) for a cooling application. Five out of the nine working pairs show no possible intermediate pressure generator refrigerant outlet temperature (\( T_{12} \)) for the operating conditions: \( T_{\text{CON}}=40^\circ\text{C}, T_{\text{ABS}}=40^\circ\text{C}, T_{\text{HPG}}=180^\circ\text{C} \) and \( T_{\text{EVA}}=5^\circ\text{C} \). Based on the vapor liquid equilibrium data and their corresponding NRTL parameters, they would not be suitable.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>( T_{12_{\text{min1}}} ) [°C]</th>
<th>( T_{12_{\text{min2}}} ) [°C]</th>
<th>( T_{12_{\text{max}}} ) [°C]</th>
<th>Range [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bmim][BF4]</td>
<td>92.5</td>
<td>103.1</td>
<td>109.7</td>
<td>6.7</td>
</tr>
<tr>
<td>[Bmim][PF6]</td>
<td>98.0</td>
<td>94.8</td>
<td>90.9</td>
<td>none</td>
</tr>
<tr>
<td>[Emim][BF4]</td>
<td>93.8</td>
<td>97.4</td>
<td>100.2</td>
<td>2.9</td>
</tr>
<tr>
<td>[Emim][EtOSO3]</td>
<td>92.7</td>
<td>81.3</td>
<td>68.6</td>
<td>none</td>
</tr>
<tr>
<td>[Emim][SCN]</td>
<td>95.9</td>
<td>105.5</td>
<td>111.7</td>
<td>6.3</td>
</tr>
<tr>
<td>[Emim][Tf2N]</td>
<td>98.1</td>
<td>97.0</td>
<td>95.2</td>
<td>none</td>
</tr>
<tr>
<td>[Hmim][BF4]</td>
<td>128.2</td>
<td>95.0</td>
<td>72.0</td>
<td>none</td>
</tr>
<tr>
<td>[Mmim][DMP]</td>
<td>87.9</td>
<td>98.6</td>
<td>110.7</td>
<td>12.1</td>
</tr>
<tr>
<td>[Omim][BF4]</td>
<td>105.9</td>
<td>92.9</td>
<td>79.8</td>
<td>none</td>
</tr>
</tbody>
</table>

Table 3.6: Range of \( T_{12} \) for a heating application. Similar to the cooling application, five out of the nine working pairs show no possible intermediate pressure generator refrigerant outlet temperature (\( T_{12} \)) for the conditions: \( T_{\text{CON}}=T_{\text{ABS}}=45^\circ\text{C}, T_{\text{HPG}}=180^\circ\text{C} \) and \( T_{\text{EVA}}=10^\circ\text{C} \). Based on the vapor liquid equilibrium data and their corresponding NRTL parameters, they would not be suitable.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>( T_{12_{\text{min1}}} ) [°C]</th>
<th>( T_{12_{\text{min2}}} ) [°C]</th>
<th>( T_{12_{\text{max}}} ) [°C]</th>
<th>Range [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bmim][BF4]</td>
<td>97.0</td>
<td>105.7</td>
<td>111.3</td>
<td>5.7</td>
</tr>
<tr>
<td>[Bmim][PF6]</td>
<td>102.4</td>
<td>98.6</td>
<td>94.2</td>
<td>none</td>
</tr>
<tr>
<td>[Emim][BF4]</td>
<td>98.5</td>
<td>100.9</td>
<td>102.8</td>
<td>1.9</td>
</tr>
<tr>
<td>[Emim][EtOSO3]</td>
<td>98.2</td>
<td>84.9</td>
<td>70.4</td>
<td>none</td>
</tr>
<tr>
<td>[Emim][SCN]</td>
<td>99.8</td>
<td>108.3</td>
<td>113.8</td>
<td>5.5</td>
</tr>
<tr>
<td>[Emim][Tf2N]</td>
<td>102.3</td>
<td>100.5</td>
<td>98.2</td>
<td>none</td>
</tr>
<tr>
<td>[Hmim][BF4]</td>
<td>129.3</td>
<td>98.7</td>
<td>76.7</td>
<td>none</td>
</tr>
<tr>
<td>[Mmim][DMP]</td>
<td>92.9</td>
<td>102.1</td>
<td>112.3</td>
<td>10.2</td>
</tr>
<tr>
<td>[Omim][BF4]</td>
<td>110.8</td>
<td>97.1</td>
<td>83.8</td>
<td>none</td>
</tr>
</tbody>
</table>

Figure 3.8 shows the COP of the cycle for different absorber and condenser temperatures using the ionic liquid [Bmim][BF4]. As expected, for lower absorber and condenser temperatures the system has a higher performance. This is because a higher condenser temperature gives a higher condenser pressure resulting in a higher concentration of stream 15, meaning less ammonia can be evaporated in the intermediate pressure generator. Increasing the absorber temperature results in lower strong solution concentration (stream 4) because higher temperatures give a lower ammonia concentration. A lower strong solution concentration gives a lower COP because there is less ammonia to be evaporated in the high pressure generator. For every absorber temperature there is a minimum and maximum \( T_{\text{HPG}} \) for which the cycle can run. If the temperature becomes lower than this limit, the restriction from equation 3.19 will be violated. That is, the concentration of the solution leaving the high pressure generator exceeds that of the entering solution. The maximum driving temperature is because of one the assumptions of the thermodynamic model, ammonia has to be at saturated conditions at stream 12, meaning that the temperature cannot exceed the critical point of ammonia at this point. Furthermore, there is an optimum \( T_{\text{HPG}} \) for every curve. If the absorber and condenser are connected in series with the external fluid, it is important to choose the best performing configuration. Figure 3.8 should be used to accomplish that. If the absorber exchanges heat with the environment at 40°C and the condenser at 30°C, for a \( T_{\text{HPG}} \) of 220°C, the COP is 0.84. Switching
3.4. Results and discussion

Table 3.7: The densities of [Bmim][BF4] for the investigated absorber temperature range. The densities change less than 0.1% for the investigated pressure range and they are considered to be temperature dependent only. Experimental data is taken from Matkowska and Hofman [19].

<table>
<thead>
<tr>
<th>$T_{ABS}$ [°C]</th>
<th>Density [$kg/m^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1198</td>
</tr>
<tr>
<td>35</td>
<td>1194.5</td>
</tr>
<tr>
<td>40</td>
<td>1191</td>
</tr>
<tr>
<td>45</td>
<td>1187.5</td>
</tr>
</tbody>
</table>

the condenser and absorber, so $T_{ABS}$=30°C and $T_{CON}$=40°C, results in the same COP. However, in accordance with figure 3.8 for a lower driving heat (e.g. $T_{HPG}$=180°C), having the absorber solution outlet at a lower temperature than the condenser outlet can improve the performance by 10%.
The COP for the given conditions and $T_{CON} = 30^\circ C$ (b) The COP for the given conditions and $T_{CON} = 35^\circ C$

(c) The COP for the given conditions and $T_{CON} = 40^\circ C$
(d) The COP for the given conditions and $T_{CON} = 45^\circ C$

Figure 3.8: The COP of the double effect absorption cycle as a function of the driving temperature for different condenser and absorber temperatures. For the condition $T_{EVA} = 5^\circ C$ using [Bmim][BF4] as absorbent. The diagram can be used as a guide for selecting the best way to connect the absorber and condenser with the external fluid to exchange heat.

Figure 3.9 shows the influence of the evaporation temperature on the COP of the double-effect absorption cycle. The trend shows that having a higher evaporation temperature increases the performance of the cycle. Furthermore, there seems to be an optimum temperature for every curve. For lower evaporation temperatures the optimum $T_{HPG}$ cannot be reached because the critical temperature of ammonia will be exceeded. Having a high evaporation temperature results in a high evaporator pressure. Consequently, the strong solution concentration will become higher, so more ammonia can be evaporated in the high pressure generator. The cycle seems to be suitable for cooling applications down to approximately -5 $^\circ C$ because there is a realistic range of operation.

The effect of the driving temperature on the concentration of the solution through the cycle is shown in figure 3.10. As expected, the highest concentration level is constant because this is independent of the driving temperature. Both the intermediate and the weakest concentration levels decrease with increasing temperature. For instructive purposes, the lower limit of the driving temperature is exceeded to see what will happen to the concentrations. Predictably, restrictions from equations 3.18-3.20 are violated and the strong concentration gets surpassed by the weakest and intermediate concentration.

Having a large concentration difference increases the cooling load but at the same time this requires more heat input in the high pressure generator. This effect can clearly be seen in figure 3.11.
3.4. Results and discussion

![Graph showing COP as a function of Thpg (°C) for different evaporation temperatures.](image)

Figure 3.9: The COP of the double effect absorption cycle as a function of the driving temperature for different evaporation temperatures. For the conditions: $T_{CON} = 40$ °C, $T_{EVA} = 30$ °C, using [Bmim][BF4] as absorbent. For lower evaporation temperatures the minimum temperature of the high pressure generator solution outlet becomes very high, this narrows down the scope of possible applications.

The driving heat and evaporator heat increase at approximately the same rate with increasing driving temperature. Furthermore, the pump power also increases because the pressure difference becomes larger with increasing driving temperature.

All the properties [Bmim][BF4] and ammonia at all the points in the cycle for the conditions $T_{ABS}=30$, $T_{CON}=40$ °C, $T_{EVA}=5$ °C and $T_{HPG}=220$ °C are listed in table 3.9. The COP and heat flows are listed in table 3.10. The results show that it is necessary to take the pump power into account, as this can decrease the performance up to 10%. The performance is better than the ammonia water working pair in the double-effect cycle for evaporation temperatures at 0 °C or below but higher driving temperatures are needed, as can be seen in table 3.8. However, for evaporation temperatures above 0 °C, the lithium bromide working pair reaches a higher COP.

Table 3.8: Performance comparison of the best performing ionic liquid based working pair and ammonia and water.

In the double-effect absorption cycle in series configuration. As can be seen, the ionic liquid reaches a higher COP than water as absorbent but the required high pressure generator temperature is higher.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ammonia / [Bmim][BF4]</th>
<th>Ammonia / water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{EVA}$</td>
<td>0 °C</td>
<td>0 °C</td>
</tr>
<tr>
<td>$T_{ABS}=T_{CON}$</td>
<td>30 °C</td>
<td>30 °C</td>
</tr>
<tr>
<td>$T_{HPG}$</td>
<td>194 °C</td>
<td>138 °C</td>
</tr>
<tr>
<td>COP</td>
<td>0.869 [-]</td>
<td>0.829 [-]</td>
</tr>
</tbody>
</table>
Figure 3.10: The three ammonia concentration levels in the solution flow of the double-effect absorption cycle as a function of the driving temperature. For the conditions: $T_{\text{ABS}} = 40 \, ^\circ\text{C}$, $T_{\text{CON}} = 30 \, ^\circ\text{C}$ and $T_{\text{EVA}} = 5 \, ^\circ\text{C}$ using $[\text{Bmim}][\text{BF}_4]$ as absorbent. The minimum operating temperature can be seen around $130 \, ^\circ\text{C}$, below this limit the restrictions are violated and the cycle would not work.

Table 3.9: State properties of the double effect absorption cycle during cooling using $[\text{Bmim}][\text{BF}_4]$. For the conditions: $T_{\text{ABS}} = 30 \, ^\circ\text{C}$, $T_{\text{CON}} = 40 \, ^\circ\text{C}$, $T_{\text{EVA}} = 5 \, ^\circ\text{C}$ and $T_{\text{HPG}} = 220 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>Point</th>
<th>Flow [kg/s]</th>
<th>Temp. [°C]</th>
<th>Conc.[kg/kg]</th>
<th>Pressure [bar]</th>
<th>Enthalpy [kJ/kg]</th>
<th>Quality [kg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>40.0000</td>
<td>1.0000</td>
<td>15.5517</td>
<td>535.0010</td>
<td>0.0000</td>
</tr>
<tr>
<td>2</td>
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<td>5.0000</td>
<td>1.0000</td>
<td>5.1571</td>
<td>535.0010</td>
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</tr>
<tr>
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<td>1.0000</td>
<td>5.1571</td>
<td>1612.3436</td>
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<tr>
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<td>5.1571</td>
<td>98.0216</td>
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</tr>
<tr>
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<td>0.0886</td>
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<td>450.5271</td>
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<td>1115.2148</td>
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<td>15</td>
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<tr>
<td>17</td>
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<td>0.0155</td>
<td>5.1571</td>
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</tr>
</tbody>
</table>
Figure 3.11: The heat flow of the evaporator, the high pressure generator and pumping power of the double effect absorption cycle as a function of the driving temperature. For the conditions: \( T_{ABS} = 40 \) °C, \( T_{CON} = 30 \) °C and \( T_{EVA} = 5 \) °C using [Bmim][BF4] as absorbent. For lower temperatures it can be seen that the pump power has a large contribution, the power needed for the pump is almost 25 % of the cooling power at 140 °C.

Table 3.10: Results obtained from the model for a cooling application using [Bmim][BF4]. For the conditions: \( T_{ABS} = 30 \), \( T_{CON} = 40 \) °C, \( T_{EVA} = 5 \) °C and \( T_{HPG} = 220 \) °C.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{EVA} )</td>
<td>79.96</td>
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</tr>
<tr>
<td>( Q_{ABS} )</td>
<td>120.93</td>
<td>kW</td>
<td>Heat flow in the absorber</td>
</tr>
<tr>
<td>( Q_{CON} )</td>
<td>53.73</td>
<td>kW</td>
<td>Heat flow in the condenser</td>
</tr>
<tr>
<td>( Q_{HPG} )</td>
<td>84.32</td>
<td>kW</td>
<td>Heat added to the high pressure generator</td>
</tr>
<tr>
<td>( Q_{IPG} )</td>
<td>45.05</td>
<td>kW</td>
<td>Heat exchanged in the intermediate pressure generator</td>
</tr>
<tr>
<td>( W_{PUMP} )</td>
<td>10.38</td>
<td>kW</td>
<td>Pump power</td>
</tr>
<tr>
<td>( COP_{cooling} )</td>
<td>0.84</td>
<td>[-]</td>
<td>COP for cooling</td>
</tr>
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</table>
3.4.4. Performance prediction for heating applications

Three ionic liquid absorbents are investigated for the performance prediction of a heating application. The performance of the workings pairs is shown in figure 3.12. As expected from the investigation of the range of $T_{12}$ in table 3.6, [EMIM][SCN] has the smallest operating range. Furthermore, for the heating application the performances of the working pairs are much closer to each other at higher driving temperatures. The ionic liquid [Bmin][BF4] reaches the highest COP again. The state properties and the results of [Bmin][BF4] during a heating application for the conditions $T_{EVA}=10^\circ$, $T_{CON}=45^\circ$, $T_{ABS}=35^\circ$ and $T_{HPG}=210^\circ$ are shown in tables 3.11 and 3.12. The pumping power is included in these results and the COP is calculated by equation 3.27

$$\text{COP}_{\text{heating}} = \frac{Q_{\text{ABS}} + Q_{\text{CON}}}{Q_{\text{HPG}} + W_{\text{PUMP}}} \quad (3.27)$$

![Figure 3.12: The COP of the double effect absorption cycle as a function of the driving temperature. For the conditions: $T_{ABS} = 35^\circ$, $T_{CON} = 45^\circ$, and $T_{EVA} = 10^\circ$ using three of the ionic liquids as absorbent. The ionic liquid [Bmin][BF4] shows the best performance for the investigated temperature range.](image)
Table 3.11: State properties of the double effect absorption cycle during a heating application using [Bmim][BF4]. At conditions: $T_{ABS} = 35$, $T_{CON} = 45$ °C and $T_{EVA} = 10$ °C and $T_{HPG} = 210$ °C.

<table>
<thead>
<tr>
<th></th>
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</thead>
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<tr>
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<td>0.0407</td>
<td>99.9576</td>
<td>232.4781</td>
<td>0.0000</td>
</tr>
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<td>105.9840</td>
<td>0.0407</td>
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<td>1.0000</td>
<td>99.9576</td>
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<td>13</td>
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<td>17.8240</td>
<td>1064.2846</td>
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<td>0.0232</td>
<td>17.8240</td>
<td>251.6178</td>
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<td>16</td>
<td>0.9272</td>
<td>46.6348</td>
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<td>116.7479</td>
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<td>17</td>
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<td>46.6211</td>
<td>0.0232</td>
<td>6.1497</td>
<td>116.7479</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table 3.12: Results obtained from the model for a heating application using [Bmim][BF4]. For the conditions: $T_{ABS} = 35$, $T_{CON} = 45$ °C, $T_{EVA} = 10$ °C and $T_{HPG} = 210$ °C.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{EVA}$</td>
<td>76.95</td>
<td>[kW]</td>
<td>Heat flow in the evaporator</td>
</tr>
<tr>
<td>$Q_{ABS}$</td>
<td>117.32</td>
<td>[kW]</td>
<td>Heat flow in the absorber</td>
</tr>
<tr>
<td>$Q_{CON}$</td>
<td>49.40</td>
<td>[kW]</td>
<td>Heat flow in the condenser</td>
</tr>
<tr>
<td>$Q_{HPG}$</td>
<td>80.08</td>
<td>[kW]</td>
<td>Heat added to the high pressure generator</td>
</tr>
<tr>
<td>$Q_{IPG}$</td>
<td>44.41</td>
<td>[kW]</td>
<td>Heat exchanged in the intermediate pressure generator</td>
</tr>
<tr>
<td>$W_{PUMP}$</td>
<td>9.63</td>
<td>[kW]</td>
<td>Pump power</td>
</tr>
<tr>
<td>COP_{heating}</td>
<td>1.86</td>
<td>[-]</td>
<td>COP for heating</td>
</tr>
</tbody>
</table>
3.4.5. Influence of the design parameters on the performance

Figure 3.13 shows the influence of the pinch temperature of HEX1, HEX2 and the intermediate pressure generator on the performance. From the figure it can be concluded that the pinch temperatures of the heat exchangers have a stronger effect on the performance than that of the intermediate pressure generator. If the pinch temperature increases in HEX1 and HEX2, the temperature of the solution entering the high pressure generator will be lower. In that case, the high pressure generator will require more heat input in order to have the same outlet temperature which reduces the performance, explaining the negative slope in figure 3.13.

![Figure 3.13: The influence of the pinch temperature.](image)

**Figure 3.13: The influence of the pinch temperature.** In the intermediate pressure generator and the first and second solution heat exchangers on the COP of the cycle as a function of the high pressure generator solution outlet temperature. For the conditions: $T_{ABS} = 40^\circ C$, $T_{CON} = 30^\circ C$ and $T_{EVA} = 5^\circ C$ using [Bmim][BF4] as absorbent.
3.5. Recommendations

3.5.1. Conclusions

• The double-effect absorption cycle using ammonia and water with rectifiers for the conditions $T_{ABS}=30 \, ^\circ C$, $T_{CON}=30 \, ^\circ C$ and $T_{EVA}=0 \, ^\circ C$ has a COP of 0.83, whereas ammonia and [Bmim][BF4] has a COP of 0.87. For lower evaporation temperatures, this performance difference becomes even larger. Additionally, using ionic liquid as absorbent has the preference because there is no need for rectifiers, thus it is a much simpler construction.

• The pump power has a strong influence on the performance. For some cases, the required pump power can decrease the COP with 10%. This is because there is a large pressure difference compared to the ammonia water working pair which would be a design challenge.

• For evaporation temperatures above 0 °C, the performance of the double-effect cycle in series configuration using the investigated ionic liquids cannot compete with the performance of the lithium bromide and water working pair.

3.5.2. Recommendations

• In this research, the mixing enthalpy is assumed to be zero. In reality, this is not zero and the effect on the performance of the cycle should be investigated.

• The effect of the viscosity of the ionic liquid ammonia mixture on the pump power, and thus the performance on the cycle, should be investigated.
4

Method to determine the excess enthalpy for ionic liquid and ammonia mixtures

4.1. Introduction

In this chapter, a method is proposed to measure the excess enthalpy of an ammonia and ionic liquid mixture. First, the theory on excess properties will be explained and the experimental method is described. A way to validate the method is proposed and illustrated by an example using ammonia and water. Lastly, the recommendations are presented.

4.2. Theory

4.2.1. Excess properties

An excess property, $M^E$, is the difference between the actual property of a solution and the property of the ideal solution at a given temperature, pressure and composition:

$$M^E = M - M^{id}$$  \hspace{1cm} (4.1)

For a binary mixture, the property of mixing is defined as:

$$M^E = M - x_a M_a - x_b M_b$$  \hspace{1cm} (4.2)

Where the subscripts $a$ and $b$ denote the pure components.

4.2.2. Mixing two liquids

If two pure liquids are mixed under the condition of constant pressure, the change in the total enthalpy is the excess enthalpy. In this case, the heat released or absorbed by the two liquids during mixing can be measured directly. Then the excess enthalpy can be calculated by [27]:

$$H^E = \frac{Q}{m}$$  \hspace{1cm} (4.3)

Where $Q$ is the heat released or absorbed and $m$ the total mass of the sample.
4. Method to determine the excess enthalpy for ionic liquid and ammonia mixtures

4.2.3. Mixing a liquid with two-phase volume

If we consider the system as illustrated in figure 4.1, where on the left side we have a two-phase region in equilibrium of pure fluid A, and on the right side a pure liquid B which are separated by a non-permeable wall. The system is at uniform and constant temperature $T$ and pressure $P$. If the non-permeable wall is removed, the two-phase region and the liquid will start mixing and a new equilibrium is formed with a new pressure and temperature. And again, the heat released or absorbed by the system can be measured directly, from which the excess enthalpy can be calculated. However, in this case the gas phase of fluid A has an effect on the excess enthalpy due to condensation/evaporation and absorption/desorption to or from the liquid phase.

4.2.4. Ionic liquid and ammonia

Now if we think of the case where we would mix ammonia with an ionic liquid we can make some assumptions. In a two phase equilibrium of ammonia and ionic liquid we can assume that the vapor pressure of the ionic liquid is negligible and ammonia has a high solubility in ionic liquid [36]. So if we consider the system illustrated by figure 4.1, after taking away the non-permeable wall we can assume that a part of the ammonia will get absorbed by the ionic liquid and that the vapor phase is pure ammonia. The mole-based enthalpy of mixing can be determined by:

$$\tilde{h}^E = \frac{Q}{n_{IL} + n_{NH_3,l}}$$  \hspace{1cm} (4.4)

Where $Q$ is the heat released or absorbed by the system during mixing and $n_{NH_3,l}$ is the amount of ammonia absorbed by the ionic liquid. Or the mass-based enthalpy of mixing by:

$$h^E = \frac{Q}{m_{IL} + m_{NH_3,l}}$$  \hspace{1cm} (4.5)

4.3. Method

4.3.1. Introduction

This method measures the mixing enthalpy for two fluids at a certain pressure, temperature and composition. Before mixing, the fluids can be in single phase or in two-phase. The method makes use of two connected volumes, each consisting of a pure fluid, that are connected by a valve that
is initially closed. By means of a thermostatic bath the samples (or volumes) will be brought to the desired temperature, after which the valve will be opened. The fluids will start mixing and the heat released or absorbed by this mixing process will be measured, from which the excess enthalpy can be calculated. The final pressure and composition can be determined by a pressure sensor inside the connected samples.

**Set-up** The set-up consists of the following equipment:

- Temperature sensors
- Thermostatic bath filled with water
- Coupled ammonia / ionic liquid sample
- Mixer
- Insulated box filled with water

The equipment will be set-up as illustrated in figure 4.2. As can be seen, the insulated box with the connected samples is submerged into a thermostatic bath. Initially, the insulated box will be open, so all the water can flow freely into the box. The thermostatic bath will be set to the chosen experiment temperature. By waiting long enough, the water and coupled samples will reach this temperature. Then, the valves connecting the cylinder samples will be opened and the insulated box will be closed quickly. This will form a closed system, consisting of the insulated box with the water and coupled sample cylinders inside. The fluids from both sample cylinders will start mixing through the connecting T-piece from left to right and vice versa. During this mixing process the connected cylinders will exchange heat with the surrounding water because of the excess enthalpy. In the case of an exothermic process, the temperature of the water in the insulated box will increase. Using the temperature increase of the water, the heat released by the samples can be calculated. To determine the total amount of water inside the insulated box, the box and samples have to be measured with and without water inside. Before, during and after the mixing process the temperature and pressure of the fluids inside the samples will be monitored.
4.3.2. Preparation of samples

To accurately prepare the ammonia and ionic liquid samples, the following equipment is required:

- Vacuum pump
- Sample cylinders
- Connecting T-piece
- Pressurized ammonia tank
- Pressure regulating valve
- Pressure & temperature sensor

The mass of these parts will be measured. Then, the vacuum pump, the connecting T-piece and the pressurized ammonia tank are connected as in figure 4.3. The connecting T-piece and the sample cylinder are vacuumized using the vacuum pump to ensure there is no air inside. Now the sample can be filled with ammonia by setting the pressure regulating valve to the desired pressure and opening the pressurized ammonia tank. After the sample is filled with ammonia, the sample cylinder can be disconnected and weighed again, so we know exactly how much ammonia is in it. This procedure will be followed to prepare multiple ionic liquid and ammonia samples with different quantities inside. Once the samples have been made, they can be connected using the connecting T-piece to make ammonia and ionic liquid sample couples, as can be seen in figure 4.4. The valves will prevent the pure fluids from mixing. The vacuum pump and pressurized ammonia tank are available in the P&E lab of the TU Delft. The connecting T-pieces, sample cylinders and valves can be ordered from Swagelok.

4.3.3. Determination of the final composition

To determine the amount of ammonia absorbed by the ionic liquid, the vapor pressure and temperature have to be measured before and after mixing. To find the final concentration of the liquid phase $x_{NH3}$ we follow the iterative loop illustrated in figure 4.5. An initial guess of the ammonia absorbed by the ionic liquid, $m_{NH3,l}$, has to be made. With this initial guess, the volume of the liquid phase can be determined by:

$$V_l = \frac{m_{IL}}{\rho_{IL}(T,P)} + \frac{m_{NH3,l}}{\rho_{NH3,l}(T,P)}$$

(4.6)

Where the densities can be found from NIST’s Refprop database [17] and BOULDER website [22]. The excess volume has not been taken into account as this has been estimated to be less than 0.1%. The total volume is known so the volume of the gas phase can be calculated:

$$V_g = V_{tot} - V_l$$

(4.7)

With the volume of the gas phase and the density of ammonia, the amount of ammonia that is left in the gas phase can be calculated by:

$$m_{NH3,v} = \rho_g(T,P)V_g$$

(4.8)

The total amount of ammonia is known, so the new calculated mass absorbed by the liquid and the error are:

$$m_{NH3,l} = m_{NH3,tot} - m_{NH3,v}$$

(4.9)

$$Error = \frac{m_{NH3,l,\text{guess}}}{m_{NH3,l,\text{calc}}}$$

(4.10)
4.3. Method

Figure 4.3: The set-up for filling the sample cylinders. Following the ordering of the illustration the components are: 1. Pressurized Ammonia tank, 2. Vacuum pump, 3. Pressure regulated valve, 4. Ammonia sample cylinder.

Figure 4.4: A schematic illustration of the connected samples. Following the ordering of the illustration the components are: 1. Ammonia sample, 2. Ionic liquid sample, 3. Valve, 4. Connecting T-piece.
4. Method to determine the excess enthalpy for ionic liquid and ammonia mixtures

Figure 4.5: Iterative loop to determine the absorbed amount of ammonia in the liquid phase. The value of the amount of ammonia absorbed into the liquid is needed to calculate the excess enthalpy. The equations and iterative loop are solved using the software package Matlab.

Table 4.1: The conditions and properties of the example experiment. Conditions have been chosen to suit available equipment in the P&E lab, any other conditions can be chosen for these validations.

<table>
<thead>
<tr>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{exp}$</td>
<td>K</td>
<td>Experiment temperature</td>
</tr>
<tr>
<td>$P_{samp}$</td>
<td>Bar</td>
<td>Pressure inside the connected sample</td>
</tr>
<tr>
<td>$m_{NH_3}$</td>
<td>kg</td>
<td>Mass of ammonia inside the 500 ml sample</td>
</tr>
<tr>
<td>$m_{H_2O}$</td>
<td>kg</td>
<td>Mass of water inside the 250 ml sample</td>
</tr>
<tr>
<td>$x_{NH_3}$</td>
<td>kg/kg</td>
<td>Concentration of ammonia in the sample</td>
</tr>
<tr>
<td>$h_{NH_3}$</td>
<td>kJ/kg</td>
<td>Enthalpy of pure ammonia in the sample</td>
</tr>
<tr>
<td>$h_{H_2O}$</td>
<td>kJ/kg</td>
<td>Enthalpy of pure water in the sample</td>
</tr>
<tr>
<td>$h$</td>
<td>kJ/kg</td>
<td>Actual enthalpy of the mixture</td>
</tr>
<tr>
<td>$m_{H_2O,box}$</td>
<td>kg</td>
<td>Mass of the water inside the insulated box</td>
</tr>
</tbody>
</table>

Once the guessed value and the calculated value are close enough, the final concentration of the liquid phase can be calculated:

$$x_{NH_3} = \frac{m_{NH_3,I}}{m_{NH_3,I} + m_{IL}}$$

4.4. Validation

To validate the set-up, the described method should be followed to determine the excess enthalpy of, e.g., ammonia and water. The results should be compared with values from NIST’s REFPROP database. A practical example using readily available equipment and materials is shown below. In this example liquid ammonia and water will be mixed. The P&E lab has a thermostatic bath of 30x20x15 cm and sample cylinders of 250 ml and 500 ml can be ordered from Swagelok. Then, the method can be followed for the conditions and properties listed in table 4.1.

With these conditions, and using the REFPROP database, the heat released by the mixing process
4.5. Recommendations

In this chapter, a method to measure the excess enthalpy of two fluids at a certain temperature, pressure and composition has been described. The calculation procedure and needed components to do the measurements are given. Furthermore, an easy way to validate the method, using a mixture of ammonia and water, is described. Topics for further research are:

- The T-piece connecting the samples might interfere with the mixing process of the two fluids. This could cause the mixing process to be too slow. A magnetic stirrer inside the connected samples could prevent this from happening.
- Research on the influence of the propeller on the temperature of the water inside the insulated box should be conducted.
- In case of mixing a two-phase fluid with a one-phase fluid, the pressure inside the connected sample can change. The influence of a pressure change on the excess enthalpy should be investigated.

### Table 4.2: Results of the example experiment for the validation of the method.

The results of the experiment for the conditions and properties listed in table 4.1. From the temperature rise, the excess enthalpy can be determined.

<table>
<thead>
<tr>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{rel}$</td>
<td>$144.5$ [kJ]</td>
<td>Heat released during mixing process</td>
</tr>
<tr>
<td>$h^E$</td>
<td>$260.5$ [kJ/kg]</td>
<td>Excess enthalpy</td>
</tr>
<tr>
<td>$\Delta T_{box}$</td>
<td>$4.17$ [K]</td>
<td>Temperature rise of the water inside the insulated box</td>
</tr>
</tbody>
</table>

Can be calculated with:

$$Q_{rel} = m_{tot}h - m_{NH_3}h_{NH_3} - m_{H_2O}h_{H_2O}$$  \hspace{1cm} (4.12)

Then, the excess enthalpy of the ammonia water mixture can be calculated with:

$$h^E = \frac{Q_{rel}}{m_{tot}}$$  \hspace{1cm} (4.13)

For the given conditions and volumes, the temperature rise should be close to the value listed in table 4.2.
5.1. Introduction

Diesel engine combustion produces pollutants like $SO_x$ and $NO_x$ and approximately 3.3% of global $CO_2$ emissions are caused by shipping [10]. The refrigeration plant on fishing ships is the largest electricity consumer onboard. It is therefore logical to find ways to reduce the primary energy used for refrigeration. On board of a fishing vessel the main engine is a source of high temperature waste heat through the exhaust gas. The heat stored in this gas can be converted into cooling power to refrigerate the fish. The combination of a high temperature heat source and the need for cooling on fishing vessels present the perfect circumstances for absorption refrigeration.

Figure 5.1: A typical trawler fishing vessel.
5.2. Demand

The studied ship is a trawler fishing vessel which is mainly used to catch mackerel and herring. In order to cool and freeze the fish on-board, the vessel is equipped with three different refrigeration plants. The biggest energy consumers are the refrigerated seawater system (RSW), the chilled water plant (CWP) and the freezing plant. The chilled water plant is designed to cool down $47 \text{ m}^3/\text{h}$ of seawater with a temperature of $32 \, ^\circ \text{C}$ to a temperature of $-1 \, ^\circ \text{C}$. This plant makes use of two screw compressors with a combined cooling power capacity of $1760 \, \text{kW}$. The chilled water plant is turned on most of the time. The refrigerated seawater plant is designed to pre-cool fish to a temperature of $0 \, ^\circ \text{C}$. It also makes use of two screw compressors with a combined cooling capacity of $2828 \, \text{kW}$. Furthermore, the freezing plant is used to freeze mackerel and herring. It has the capacity to freeze 400 tons of mackerel or 460 tons of herring per 24 hours while maintaining the temperature of the holds at $-30 \, ^\circ \text{C}$ using 10 screw compressors. The freezing plant has an effective cooling capacity of $2400 \, \text{kW}$. Table 5.1 lists when each refrigeration plant is turned on for every operating mode. Table 5.2 lists the cooling demands and the cooling temperatures. The vessel requires a total of $6982 \, \text{kW}$ cooling power.

Table 5.1: The refrigeration plants and when they are turned on for the different operating modes.

<table>
<thead>
<tr>
<th>Operating Mode</th>
<th>RSW</th>
<th>CWP</th>
<th>Freezing plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fishing with production</td>
<td>On</td>
<td>On</td>
<td>On</td>
</tr>
<tr>
<td>Fishing without production</td>
<td>On</td>
<td>Off</td>
<td>Off</td>
</tr>
<tr>
<td>Sailing to fishing zone and tracking down fish</td>
<td>On</td>
<td>Off</td>
<td>Off</td>
</tr>
<tr>
<td>Retrieving or placing nets, pumping fish on board</td>
<td>On</td>
<td>On</td>
<td>On</td>
</tr>
<tr>
<td>Out of order or unloading fish</td>
<td>Off</td>
<td>Off</td>
<td>Off</td>
</tr>
</tbody>
</table>

Table 5.2: The cooling power and electric power consumption of the three refrigeration plants.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Cooling power demand $[\text{kW}]$</th>
<th>Electric power consumption $[\text{kW}]$</th>
<th>Cooling temperature $[\text{°C}]$</th>
<th>$T_{ABS} = T_{CON}$ $[\text{°C}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSW</td>
<td>2828 (2x 1414)</td>
<td>1068</td>
<td>-1</td>
<td>-6</td>
</tr>
<tr>
<td>CWP</td>
<td>1760 (2x 880)</td>
<td>577</td>
<td>-1</td>
<td>-6</td>
</tr>
<tr>
<td>Freezing plant</td>
<td>2400</td>
<td>4610</td>
<td>-30</td>
<td>-35</td>
</tr>
</tbody>
</table>
5.3. Model

The process flow diagram of the model used to do the cycle calculations is displayed in figure 5.2. The absorber and condenser exchange heat with the seawater and the high pressure generator uses the heat from the exhaust gas from the Diesel engine to evaporate ammonia from the solution. The ionic liquid [Bmim][BF₄] is used as absorbent as this ionic liquid performed best in previous research. The equations and the calculation procedure of the cycle are described in chapter 3.

![Figure 5.2: Process flow diagram of the double-effect absorption cycle in a series configuration.](image)

5.4. Results

5.4.1. Cooling power potential

The fishing vessel is equipped with a 7920 kW Wartsila Diesel engine. The high temperature heat stored in the exhaust gas from this engine can be used as input power for absorption refrigeration. Depending on the operating mode, the engine runs at different loads. The temperature and the mass flow of the flue gas are dependent on the load of the engine. Table 5.3 lists the properties of the exhaust gas for different engine loads over the period of a year. The majority of the time the vessel operates at 90 % load during which it has a significant higher exhaust gas mass flow than at lower loads and thus more recoverable heat. To prevent risk of sulfur corrosion, the exhaust gas cannot be cooled down below 167 °C [28]. In the high pressure generator a pinch temperature of 10 K is assumed which means that \( T_7 \) will always be higher than 157 °C.

Equation 5.1 is used to calculate the recoverable heat from the flue gas. The amount of heat that can be extracted to power the double-effect absorption cycle depends on how much the exhaust gas flow can be cooled down. By increasing \( T_8 \), \( T_7 \) will also increase so the exhaust gas has a smaller temperature range over which it can be cooled. At the same time, by increasing \( T_8 \), the COP of the cycle increases until it reaches its maximum. This means that for every engine load and seawater temperature there is an optimum high pressure generator solution outlet temperature (\( T_8 \)) for which the potential cooling power is at its highest.
(a) The influence of $T_{HPG}$ on the COP of the cycle.  
(b) The influence of $T_{HPG}$ on the heat flows.

Figure 5.3: The performance and potential of the double-effect absorption cycle using [Bmim][BF4] and ammonia as working pair. For the conditions $T_{EVA} = -6 \, ^\circ C$ and $T_{CON} = T_{ABS} = 37 \, ^\circ C$. This corresponds to a seawater temperature of 32°C. The recoverable heat shows a negative trend with increasing $T_{HPG}$ and the potential cooling power shows a maximum at around 215 °C. Not all conditions are possible, $T_7$ must always be higher than 157 °C.

(a) The influence of $T_{HPG}$ on the COP of the cycle.  
(b) The influence of $T_{HPG}$ on the heat flows.

Figure 5.4: The performance and potential of the double-effect absorption cycle using [Bmim][BF4] and ammonia as working pair. For the conditions: $T_{EVA} = -6 \, ^\circ C$ and $T_{CON} = T_{ABS} = 21 \, ^\circ C$. This corresponds to a seawater temperature of 16°C. As expected, the COP and the potential cooling power are much higher compared to tropical seawater temperatures. For some conditions the potential cooling power is higher than the recoverable heat from the exhaust gas. Not all conditions are possible, $T_7$ must be higher than 157 °C.
Table 5.3: Properties of the flue gas coming from the 7920 kW Wartsila Diesel engine. The properties are shown for different engine loads and operating modes for a period of 1 year. The vast majority of the time the engine operates at a load of 90%.

<table>
<thead>
<tr>
<th>Engine load</th>
<th>Duration [h]</th>
<th>Exhaust gas flow [kg/s]</th>
<th>Temperature [°C]</th>
<th>Operating mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 %</td>
<td>5400</td>
<td>9.35</td>
<td>350</td>
<td>Fishing with production</td>
</tr>
<tr>
<td>90 %</td>
<td>400</td>
<td>9.35</td>
<td>350</td>
<td>Fishing without production</td>
</tr>
<tr>
<td>70 %</td>
<td>320</td>
<td>7.58</td>
<td>356.5</td>
<td>Sailing to fishing zone, tracking down fish</td>
</tr>
<tr>
<td>35 %</td>
<td>1200</td>
<td>4.57</td>
<td>365</td>
<td>Retrieving or placing nets, pumping fish on board</td>
</tr>
<tr>
<td>0 %</td>
<td>1440</td>
<td>N/A</td>
<td>N/A</td>
<td>Out of order or unloading fish</td>
</tr>
</tbody>
</table>

\[ \dot{Q}_{rec} = c_{p,ex} \dot{m}_{ex}(T_{ex} - (T_{7} + 10K)) \] (5.1)

Figure 5.3 shows the COP, the recoverable heat and the potential cooling power as a function of the high pressure generator outlet solution temperature for a seawater temperature of 32 °C (so \( T_{CON} = T_{ABS} = 37°C \)) and an engine load of 90 %. An optimum for the potential cooling power can be seen around 215 °C. The exhaust heat flow shows a negative linear trend because \( T_{7} \) increases linearly with \( T_{8} \). For higher temperatures, the COP stagnates so increasing \( T_{8} \) more will only negatively affect the potential cooling power. When choosing the optimal temperature for \( T_{8} \), one always has to check if \( T_{7} \) is not below 157 °C.

Figure 5.3 shows the performance of the cycle for a seawater temperature of 16 °C. It is clear to see that having a lower temperature for the high pressure generator solution outlet is favorable. However, this would result in the risk of sulfur condensation.

The potential cooling power for the different engine loads and seawater temperatures are listed in table 5.4 and table 5.5. The data is given for seawater temperatures of 16 °C and 32 °C because the documentation of the studied fishing ship uses these conditions. The potential cooling power at lower seawater temperatures is much higher. This large difference can be explained by three reasons. When the seawater temperature is lower, the absorber and condenser operate at a lower temperature. As explained in chapter 2, having a lower absorber and condenser temperature increases the COP of the cycle so more recovered heat from the exhaust gas can be converted into cooling power. Additionally, the optimal high pressure generator solution outlet temperature is much lower for lower seawater temperatures. This means that the exhaust gas can be cooled down more resulting in more recoverable heat. Furthermore, the pump power at lower seawater temperatures is much lower because the pressure difference between the absorber and the high pressure generator is much lower. For lower seawater temperatures, the potential cooling power would be even higher if the absorption cycle would run at lower temperatures but this would violate the minimum exhaust gas temperature for the prevention of sulfur corrosion.

The results show that for an engine load of 90 % and a seawater temperature of 16 °C the absorption cycle can supply the cooling demand for the entire chilled water plant, almost 27 % of the total cooling demand. However, for higher seawater temperatures and lower engine loads, a back-up cooling system or another heat source is needed to power the absorption cycle.
5.4.2. Influence of seawater temperature

The seawater temperature will vary depending on the location of the vessel. As mentioned before, the seawater temperature has a very strong influence on the performance. Figure 5.5a shows the COP of the cycle as a function of the seawater temperature. The COP shows a strong decrease with increasing seawater temperature. This means that the vessel can save more energy when fishing in a cooler climate.

Figure 5.5b shows the potential cooling power and the recoverable heat from the exhaust gas as a function of the seawater temperature. Both show a strong decrease with increasing seawater temperature. However, for a seawater temperature of 35 °C the cycle could still provide the cooling demand of one of the screw compressors (880kW) used for the chilled water plant.
5.5. Conclusions and recommendations

In this chapter the suitability of absorption refrigeration for the cooling of fish on a fishing vessel is investigated. The thermodynamic model described in chapter 3 uses the heat stored in the exhaust gas coming from the Diesel engine of the vessel and converts it to cooling power. With this model, the potential cooling power that the double-effect effect absorption refrigeration cycle using ammonia and \[\text{[Bmim][BF4]}\] as working pair can supply for two different climates has been calculated. The influence of the high pressure generator operating temperature and the seawater temperature on the performance on the cycle is described.

5.5.1. Conclusions

- The double-effect effect absorption refrigeration cycle using ammonia and \[\text{[Bmim][BF4]}\] as working pair can supply the needed cooling power for the entire chilled water plant for a engine load of 90 % and when the seawater temperature is 16 °C. However, for certain conditions, the cooling power from the existing refrigeration plant is still needed. Hence, the cycle should be used as an auxiliary refrigeration plant, where the screw compressors can be turned off during the right conditions.

- The seawater temperature has a very strong effect on the performance of the cycle, and thus the amount of energy that can be saved. When the seawater temperature increases with 20 K, the amount of potential cooling power decreases with approximately 50 %.

5.5.2. Recommendations

- In order to give an accurate estimation of how much energy can be saved during a year, data of the variation of the seawater temperature during a journey of the vessel is needed.

- The influence of vessel movements and vibrations on the performance of the cycle should be investigated.

- The corrosive effect of seawater on the heat exchangers and the power needed to pump the
seawater through them should be investigated.

- The size and cost of the double-effect absorption cycle on the vessel should be evaluated.
- A dynamic study should be done.
Conclusions and outlook

Firstly, a thermodynamic model of a double-effect absorption cycle in series configuration was used to predict the performance and suitability of the ammonia and water working pair. The effect of the operating conditions, design parameters and the influence of the rectifiers needed to purify the refrigerant was investigated. To predict the performance of nine ionic liquids as absorbents, their vapor-liquid equilibrium and enthalpy, derived from heat capacities, were correlated using experimental data. With the correlations and the thermodynamic model of the double-effect absorption cycle in series configuration, the performance and suitability of these new working pairs were investigated. However, in order to give accurate predictions of the performance of the ionic liquids, excess enthalpy data is needed. Thus, a method to measure the excess enthalpy of these working pairs was proposed. Lastly, the potential of using the ionic liquid [Bmim][BF4] and ammonia as working pair in double-effect absorption cycles on board of a fishing vessel for the refrigeration of fish was studied.

6.1. Conclusions

• For the investigated operating conditions, the ionic liquids [Bmim][BF4], [Mmim][DMP] and [Emim][SCN] used as absorbents in the double-effect absorption cycle reached the best performance.

• Ammonia and the best performing ionic liquids show promise as a potential working pair for the double-effect cycle in series configuration. For an evaporation temperature of 0 °C and when a high temperature heat source is available, the proposed working pairs perform better than ammonia and water in the double-effect cycle.

• For evaporation temperatures above 0 °C, ammonia based cycles are not as good as the ones that use water as refrigerant.

• The refrigeration of fish on fishing vessels could be a promising application for the double-effect absorption refrigeration cycle using ammonia and ionic liquids as working pairs. For an engine load of 90 % and a seawater temperature of 16 °C, 27 % of the entire cooling demand needed by a large trawler fishing vessel could be supplied by absorption refrigeration.
6.2. Outlook

- In order to give accurate predictions of the performance of the investigated ionic liquid absorbents using ammonia as refrigerant, experimental data of the mixing enthalpy of the ammonia and ionic liquid working pairs is needed and the effect of the viscosity on the performance of the cycle should be investigated. Ionic liquid and ammonia working pairs have never been used in an actual experimental absorption cycle set-up. This would be the next big step towards the realization of actual functional absorption cycles using this new working pair.

- Absorption refrigeration on fishing vessels has potential but many challenges exist. Not much is known about the influence of movements and vibrations of the vessel on the performance of absorption refrigeration cycles. Additionally, because space on a ship is limited, the required dimensions of the system have to be evaluated and an estimation of the investment costs should be made.


