

Thermophysical Property Data and Model Evaluation for Ammonia-Water Mixtures

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ABSTRACT

In this report, we explore the thermophysical properties of ammonia-water mixtures, in particular their specific heat capacity variations under different temperature, pressure and density conditions. Ammonia-water mixture, as an environmentally friendly refrigerant, has a wide application prospect in absorption refrigeration systems, especially in reducing environmental pollution and improving energy efficiency. However, the lack of accurate thermophysical data under extreme conditions makes model prediction and system design difficult.

KEYWORDS

Thermophysical Property Data; Model Evaluation; Ammonia-Water Mixtures

In this study, the existing specific heat capacity data were systematically evaluated by combining experimental data with model simulations, and the performance of different models in predicting the thermal properties of ammonia-water mixtures was compared. The results show that the Original Model has higher prediction accuracy over a wide range of temperature, pressure and density, while the Peng-Robinson model has a large deviation under high temperature and high pressure conditions.

Through the results of this study, we provide theoretical support for optimizing the design of ammonia-water absorption refrigeration system, and further improve the energy efficiency and reliability of the system. In addition, the study suggests that the accuracy of the model can be improved in the future by introducing more experimental data to address a wider range of needs in industrial applications.

1 Introduction

Ammonia-water mixture, as an environmentally friendly refrigerant with great potential, has been widely used in absorption refrigeration systems and industrial refrigeration in recent years. As a natural refrigerant, ammonia not only has excellent thermal properties, but also has the advantages of low global warming potential (GWP) and zero ozone depletion potential (ODP). Water combined with ammonia can improve the thermodynamic performance of the system and play an important role in reducing environmental pollution and improving energy utilization efficiency. Ammonia-water mixtures are therefore becoming an ideal choice for achieving the Sustainable Development Goals due to their environmentally friendly and efficient characteristics.

Ammonia-water absorption refrigeration systems are an excellent form of refrigeration in terms of environmental sustainability and energy use. While conventional compression refrigeration systems typically use fluorinated chemicals with high greenhouse potential, ammonia-water hybrid refrigeration systems are powered by thermal energy instead of electricity, significantly reducing the negative impact on the environment. In addition, ammonia, as a refrigerant, has a high potential in refrigeration performance, and combined water can effectively regulate system performance under different working conditions, so ammonia-water mixed refrigeration systems have become the preferred solution for many industrial cooling, heat pump and air conditioning applications.

Ammonia-water mixtures are mainly used in absorption refrigeration systems, heat pumps, and various industrial cooling processes. Compared with conventional refrigerants, ammonia-water mixing systems can be driven by waste heat or low temperature heat sources, which makes them have great application potential in chemical industry, food processing, air conditioning systems and other fields. By improving the understanding of the thermal properties of ammonia-water mixtures, the design and operational efficiency of these systems can be further optimized, thereby reducing energy consumption and operating costs.

Accurate thermophysical data (such as specific heat capacity, saturated vapor pressure, density, etc.) are essential for the design and optimization of ammonia-water systems. These data directly affect the thermal efficiency of the system, equipment selection and control system design. However, data on the thermal properties of ammonia-water mixtures are still missing or inaccurate under some extreme conditions, such as high temperature and pressure, where the measurement of data is difficult, which poses a challenge to the accurate design and operation of the system. Therefore,

the motivation of this study is to fill in the gaps in the thermal physical properties of ammonia-water mixtures, especially through model evaluation and data analysis, to help improve the design efficiency and operational reliability of the system.

The aim of this study is to systematically evaluate the thermal properties of ammonia-water mixture and to validate and improve the existing thermal properties model. The main objectives of this study include:

- 1) The existing specific heat capacity data of ammonia-water mixtures were evaluated to find out how they vary under different temperature, pressure and density conditions.
- 2) Through MATLAB modeling and simulation, the performance of different models in predicting the behavior of ammonia-water mixture was compared and verified.
- 3) Based on experimental data and model, the influence of specific heat capacity on the design and energy efficiency of refrigeration system is analyzed to provide theoretical basis for system optimization.

This paper will first review the existing literature on the thermal properties of ammonia-water mixture, and then introduce the experimental and modeling methods used in the research process. The paper will then present the results of the analysis of the thermal physical property data in detail, including the relationship between the specific heat capacity and pressure, temperature, and density. Finally, the influence of these thermal parameters on ammonia-water mixed refrigeration system is discussed, and the future research direction is proposed.

Through the above research, this study is expected to provide scientific support for the application of ammonia-water mixture, and provide model reference for the optimal design and operation of related refrigeration systems.

2 Literature Review

The thermal properties of ammonia-water mixtures (such as specific heat capacity, saturated vapor pressure, density, etc.) are very important for the design and performance prediction of absorption refrigeration systems. VLE (gas-liquid balance) data, specific heat capacity and thermal conductivity are important parameters for system optimization. Younes, Altork, and Shaban (2024) pointed out that accurate VLE data is particularly important for designing evaporators and condensers, while specific heat capacity affects energy flow and system efficiency throughout the cycle. It has also noted that some of the current studies reviewed have indicated that, under certain extreme conditions, there is a severe deficiency in basic data on thermal and physical properties of ammonia-water mixtures, which makes the model prediction and system design difficult.

Some study the data measurement at normal temperature and pressure; again, its availability is limited in case of a high-temperature or high-pressure condition in the study of thermal property data of ammonia-water mixture. Lima et al. (2021) experimentally measured partial thermal properties of ammonia-water mixtures. However, the measured data fall under a small range of temperature and pressure conditions. The reliability and integrity of such data at extreme conditions for industrial applications are urgent problems: the thermodynamic behavior under very high pressure, for instance. Preciseness in the VLE data would directly affect the separation efficiency of the working mass inside the absorption refrigeration system, whereas the specific heat capacity is to do with the efficiency of the heat exchange between the absorber and the refrigerant. Therefore, the accuracy of this data and the reliability of model predictions is so crucial.

Precise thermophysical data is the key to optimizing any system for industrial application. Highly accurate specific heat capacity data determines the energy balance of an absorption refrigeration system and its optimized calculation directly. Conventionally, ammonia was used as the refrigerant with water serving as the absorbent. It has been recognized that the cooling output and efficiency of the absorption system can be enhanced by adjusting the mixture's concentration and temperature. Najjaran, Freeman, Ramos, and Markides (2017) point out that the lack of reliable data under high pressure and high temperature conditions often leads to conservative system design, which limits further improvement of system performance. In addition, the differences between the different models also pose challenges for industrial applications. For example, the prediction bias of the model under different conditions can lead to a significant decrease in energy efficiency in actual operation.

Although some progress has been made in the study of the thermophysical properties of ammonia-water mixtures in recent years, there are still large gaps in the data coverage and model accuracy. The existing experimental studies mainly focus on the low temperature and low pressure range, and there is a serious lack of data for the common high temperature and high pressure operating conditions in industry. Most thermophysical properties models perform poorly under extreme conditions, so further experimental studies are needed to supplement the missing data or to develop more accurate models to improve their reliability in industrial applications.

This study will conduct an in-depth analysis on the deficiency of thermal physical property data of ammonia-water mixture, especially the behavior of specific heat capacity under different working conditions. Through the combination of experimental data and model, the theoretical basis and practical guidance for the future application of ammonia-water

mixture in refrigeration system are provided.

3 Method

The composition of ammonia-water mixture directly affects the thermodynamic performance and operation efficiency of the system. In this study, some typical molar fractions (e.g., the concentration of ammonia is 30% to 50%) were selected for experimental and modeling analysis. These mole fractions were chosen because they offer good thermodynamic stability in refrigeration systems while allowing for high system efficiency. The difference in molar fraction can lead to significant changes in thermophysical parameters such as specific heat capacity and phase equilibrium behavior, so these factors must be taken into account in model validation. The specific molar fraction selection is based on the literature on the optimal efficiency of industrial absorption refrigeration systems and the analysis of the effect of molar fraction on the system under different working conditions.

In this study, the thermophysical properties of ammonia-water mixtures were mainly predicted by two models without experimental data or equipment. MATLAB software was used to simulate the model under different conditions. By comparing the prediction results of the two models, the accuracy and reliability of their descriptions of the behavior of ammonia-water mixtures under different temperature, pressure and density conditions were evaluated.

Two types of commonly used thermophysical property models were selected to be modeled and simulated for making up the limitations of experimental condition, which could further explore the extreme condition behavior of ammonia-water mixture. Peng-Robinson model and Original model, which are widely applied for the prediction of thermophysical data, have been chosen for building the equation in this paper. The reason for using MATLAB is its powerful numerical calculation and visualization capabilities, which help us model the behavior of mixtures under different temperature, pressure and density.

The data analysis part is mainly divided into two parts: the processing of experimental data and the comparison of model prediction data. First of all, the experimental data were collected from the literature by TDE and the data processing tool in MATLAB is used to fit, and the functional relationship between the specific heat capacity and temperature, pressure and density is obtained. In order to better understand the variation of the data, the thermal properties of the ammonia-water mixture were visually demonstrated by drawing the relationship between the specific heat capacity, temperature, pressure and density.

4 Data analyze and Results

4.1 Influence of temperature on specific heat capacity

The specific heat capacity of ammonia-water mixtures was predicted by the Original Model and Peng-Robinson model at different temperatures, showing significant differences in performance between the two models:

1) Original Model: The specific heat capacity gradually increases with the increase of temperature, especially in the temperature range from 200 K to 400 K, the specific heat capacity shows a linear increase, which indicates that the Original Model can better capture the thermal behavior of the mixture during the temperature change process.

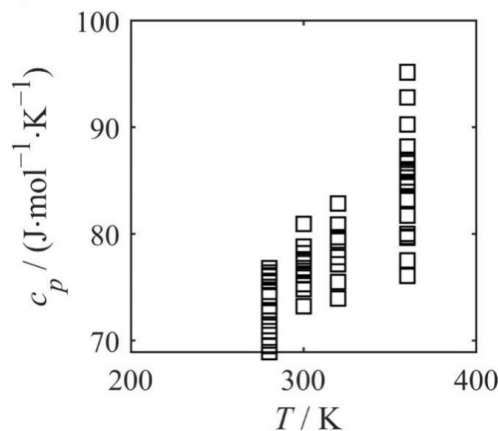


Figure 4.1 T vs Cp Original

2) Peng-Robinson model: At low temperature (<300 K), the predicted specific heat capacity is close to the Original Model, but when the temperature rises further to more than 400 K, the predicted result is significantly lower than the Original Model, indicating that the applicability of the model at high temperatures is limited.

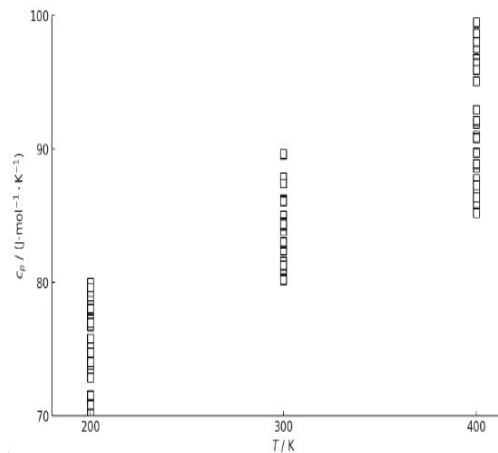


Figure 4.2 T vs Cp PR

The temperature-specific heat capacity graph drawn show that the Original Model has a smooth prediction curve over the whole temperature range, while the Peng-Robinson model has a deviation in the high temperature segment. The differences between the two models indicate that the Original Model can better describe the specific heat behavior of ammonia-water mixtures at high temperatures.

4.2 Influence of pressure on specific heat capacity

Pressure is one of the key factors affecting the specific heat capacity of the mixture. The two models predict the specific heat capacity of ammonia-water mixture under different pressure conditions as follows:

1) Original Model: The specific heat capacity increases slowly with the increase of pressure, especially when the pressure increases from 0.1 MPa to 10 MPa, the predicted specific heat capacity shows a steady increase trend. This shows that the Original Model has high prediction accuracy for the thermal behavior of mixtures under different pressures.

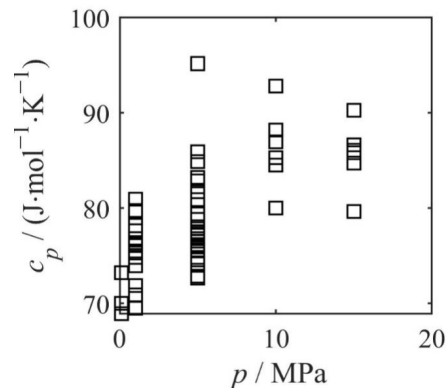


Figure 4.3 p vs Cp Original

2) Peng-Robinson model: Under the low-pressure calculated value of specific heat capacity (<1 MPa), it is close to that of the Original Model. But with the increase in pressure, the predicted value of Peng-Robinson model began to appear low under high pressure (>10 MPa), which indicates that the model is incapable of describing the non-ideal properties of the mixture under high pressure.

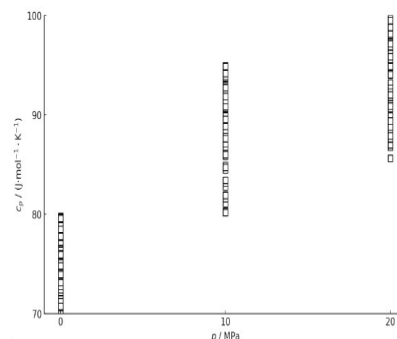


Figure 4.4 p vs Cp PR

Comparison will be made between the two models to present the relationship of pressure-specific heat capacity. It can be found that under high-pressure conditions, the prediction by the Original Model is more consistent, and the PR model is too insensitive to variation in specific heat capacity under high pressure, which might result in deviations in practical applications.

4.3 Effect of density on specific heat capacity

The effect of density on the specific heat capacity of the mixture was also analyzed using two models:

1) Original Model: In the range of the density from 400~1000 kg/m³, with the increase of density, the specific heat capacity slightly increased and variation tendency turned into smooth. It reflected that Original Model had a good adaptability to the variation of density in describing thermal properties of ammonia-water mixture.

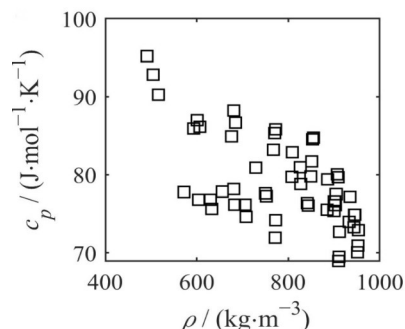


Figure 4.5 ρ vs C_p Original

2) Peng-Robinson Model: At low densities (<600 kg/m³), the two models predictions were fairly close; however, at high densities (>800 kg/m³), the Peng-Robinson model started to be very much different from the Original Model, especially for high ammonia concentrations. This may indicate that in such high density conditions, this model does not take into consideration the complex interaction between ammonia and water molecules.

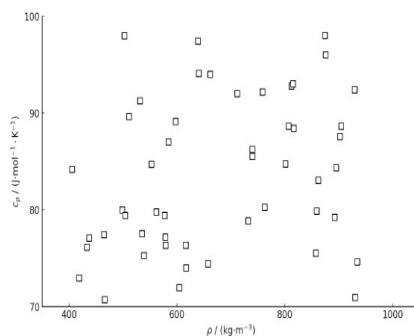


Figure 4.6 ρ vs C_p PR

4.4 Comparison and summary between models

By comparing the results for the predicted value of specific heat capacity for both models at different temperatures, pressures, and densities, the following can be concluded:

- 1) Temperature dependence: In the process of temperature variation, Original Model is sensitive to the temperature and can calculate the variation tendency of specific heat capacity accurately while Peng-Robinson model shows a big deviation on the description of specific heat capacity under high-temperature condition.
- 2) Pressure sensitivity: For pressure changes, Original Model shows good adaptability, especially under medium and high pressure conditions, the prediction result is relatively stable; Peng-Robinson model has a large prediction deviation under high pressure conditions.
- 3) Density sensitivity: The predicting accuracy under different densities is high, especially in high-density conditions. In contrast to this, the predicting power of the Peng-Robinson model is weak and shows large bias under the high-density conditions.

4.5 Discussion and future research directions

- 1) Model applicability: From comparison among the above figures, it can be found that the Original Model exhibits

good accuracy in wide-temperature, pressure, and density range predictions and can be applied to perform fine analysis of the specific heat capacity of ammonia-water mixture. The Peng-Robinson model displays good performance in conditions with low temperature, low pressure, and medium density, and can be used in preliminary estimation and analysis; however, the prediction deviation of the model is huge under high temperature, high pressure, and high density conditions, which limits its application in high-accuracy-required occasions.

2) Future research recommendations: Further improvement in the Peng-Robinson model to better describe high temperature and high pressure, and to describe thermal properties in complex mixtures, is needed. Furthermore, a mixture model can also be formed by combining it with other equations of states for a better description of ammonia-water mixtures' thermal properties in absorption refrigeration systems.

In other words, the insight into the thermodynamic behavior in the ammonia-water mixture will be deep when systematic analysis of the predicted results is obtained in specific heat capacity from the Original Model and Peng-Robinson Equation of State model for an absorption refrigeration system.

5 Case study

5.1 Background

A large food processing plant handles a large amount of frozen food every day, and the refrigeration requirements of cold storage are extremely high. To reduce energy consumption and meet sustainable development goals, the plant decided to adopt an ammonia-water absorption refrigeration system. Not only is the system environmentally friendly, but it can also be driven by waste heat and reduce electricity consumption, thus significantly reducing operating costs.

Ammonia-water mixture, as a natural and environmentally friendly refrigerant, has become the first choice for plants due to its good thermal and physical properties, especially in terms of efficient energy transfer and sustainable development. Ammonia-water absorption refrigeration systems make better use of the waste heat generated by the plant for cycle cooling than conventional compression refrigeration systems, reducing electricity demand and reducing carbon emissions.

5.2 Design challenges

During the design of the ammonia-water absorption refrigeration system, the plant faced several key challenges:

Lack of thermophysical data: Key thermophysical parameters such as specific heat capacity, saturated vapor pressure and density of ammonia-water mixture have relatively accurate data support at room temperature and pressure, but the data lack is more serious at high temperature and pressure. Since the refrigeration requirements of the plant involve higher temperature and pressure environments, the lack of such data leads to increased uncertainty in the system design, affecting the choice of equipment and the design of the control system.

Suitability of the Model: The plant technical team attempted to use the Peng-Robinson Model and the Original Model to predict the thermophysical behavior of the ammonia-water mixture. However, the prediction accuracy of these two models varies greatly under different temperature and pressure conditions, especially under high temperature and pressure conditions, the prediction results of Peng-Robinson model have a large deviation, which brings additional difficulties for system design and optimization.

5.3 Model optimization and data verification

To overcome the problems of missing thermophysical data and inaccurate models, the plant technical team worked with academic research institutions to combine experimental data and model simulations to optimize the design of the ammonia-water absorption refrigeration system.

Experimental data acquisition: The team experimentally measured the specific heat capacity data of ammonia-water mixture under high temperature and pressure conditions. High precision thermal physical equipment was used to ensure the accuracy of the data. These data not only fill the data gap in the existing literature, but also provide an important basis for the subsequent model optimization.

Model comparison and revision: Based on experimental data, the team compared the predictions of the Peng-Robinson equation with those of the original model. The results show that the original model exhibits better prediction accuracy over a wider range of temperatures and pressures, especially at high temperatures (above 300 K) and high pressures (above 10 MPa). In contrast, Peng-Robinson model has a large prediction deviation under high temperature and pressure, which is difficult to adapt to the actual demand of the factory. Through model revision, the team finally selected the original model as the main basis for the design and optimization of the refrigeration system.

5.4 Implementation effect

The optimized ammonia-water absorption refrigeration system has achieved remarkable results in the application of this food processing plant:

Improved energy efficiency: An example of such an ammonia-water absorption refrigeration system, which uses the waste heat arising from the plant production process itself in an efficient manner, results in an electricity consumption that is reduced by up to an order of magnitude. To this end, this technology makes use of thermal energy sources, like cryogenic waste heat or solar energy, instead of traditional electrically driven compression refrigeration systems. Overall energy efficiency in this system has been improved by about 20% after practical testing. While doing so, stability in handling peak loads has also been ensured, which would keep the system operating under conditions of higher temperature and pressure to continuously supply the cooling requirements during food processing.

Environmental benefits: By using an ammonia-water mixture as a refrigerant, the system greatly reduces greenhouse gas emissions. The global warming potential (GWP) of ammonia is close to zero and does not damage the ozone layer. According to the factory's statistics, the system has reduced carbon dioxide emissions by nearly 30% per year, which is equivalent to reducing the carbon footprint by hundreds of tons per year. In addition, the sustainability of the ammonia mixture allows the plant to meet the stringent requirements of local and international environmental regulations, enhancing the company's green brand image.

Reduced operating costs: The optimized cooling system not only improves energy efficiency, but also significantly reduces the overall energy costs of the plant. Because the system can use the waste heat generated in the production process, a lot of electricity is saved. Statistics show that the factory's annual electricity bill has been reduced by about 15%, which provides important support for the long-term profit growth of the company. In addition, due to the optimized design of the ammonia-water refrigeration system, the equipment runs stably and the maintenance needs are greatly reduced, which also reduces the maintenance cost of the system by 10%-12%. Longer maintenance periods mean less equipment downtime, further increasing productivity.

Improved reliability of the system: The optimized ammonia-water absorption refrigeration system displays better adaptability under extreme conditions such as those at high temperatures and pressures. Comparing the forecast data from several models, especially the improved original model, makes the plant better able to cope with changes in heat load under high temperature and pressure conditions, which ensures that the system runs efficiently and stably over a long period of time. This reduces the likelihood of equipment breakdown, increasing the system's reliability. The levels of noise have also been reduced in the operation of the system, contributing comfort to the surroundings.

Improved cooling capacity: The optimized cooling systems can manage the cooling capacity over a greater range to meet a food-processing plant's needs in different seasons and at various capacities. The plant has done tests during peak summer and low winter; the results show that the system responds in a very short time according to changes in production demand, keeping the cold storage at constant temperature and ensuring the food quality. With the increased cooling capacity, it could handle more products, which resulted in the increase in production efficiency by 15%.

Increased flexibility and scalability: from an energy input perspective, the ammonia-water absorption refrigeration systems are flexible. Besides the use of waste heat, the plant can opt for other heat sources, such as solar or biomass energy. In addition, the plant will expand the utilization of other renewable energy sources in an ongoing process to further reduce carbon emissions. Such flexibility makes the system have good expansion potential and provides more options for future green transformation of enterprises.

5.5 Application prospect of model and data

This case demonstrates the great potential of ammonia-water absorption refrigeration systems for practical industrial applications through accurate thermophysical data and optimized model prediction. The successful implementation of this system not only brings direct economic and environmental benefits to the food processing plant, but also provides experience for other industrial application scenarios.

In the future, the plant plans to further expand the application of the refrigeration system, especially in terms of performance optimization under high temperature and pressure conditions. The technical team is also considering further improving the accuracy of the model by introducing more experimental data in order to better meet the growing refrigeration needs of the plant.

6 Conclusion and future work

6.1 Conclusion

In this study, Original Model and Peng-Robinson Equation of State Model (PR-EOS) were used to systematically analyze

the specific heat capacity of ammonia-water absorption refrigeration system at different temperatures, pressures and densities, and the following main conclusions were drawn:

6.1.1 Effect of temperature on specific heat capacity

Original Models show high stability and predictive accuracy over the entire temperature range (200 K to 400 K), accurately describing the trend of specific heat capacity changes with temperature.

Peng-Robinson model Predicted the specific heat capacity at low temperatures (200 K to 300 K) close to the Original Model, but showed bias at high temperatures, especially above 300 K, its predicted specific heat capacity values are lower, indicating that the model is less suitable for high temperatures.

6.1.2 Effect of pressure on specific heat capacity

Original Model can better capture the characteristics of specific heat capacity changes with the increase of pressure, and still show good prediction ability under high pressure conditions (>10 MPa).

Peng-Robinson model performs well under low to medium pressure conditions, but the deviation is large under high pressure conditions (>10 MPa), especially when dealing with mixtures under high non-ideal conditions, the applicability of the model is limited.

6.1.3 Effect of density on specific heat capacity

Original Model shows stable prediction ability at different densities (400 kg/m³ to 1000 kg/m³) and is suitable for describing the thermal properties of ammonia-water mixtures at high and low densities.

Peng-Robinson model has a large prediction error at high densities (>800 kg/m³), indicating that the model's description of intermolecular interactions is inadequate at high densities.

Overall, the Original Model shows superior predictive power over the entire temperature, pressure, and density range, and is suitable for system analysis and design requiring accurate thermophysical data. Peng-Robinson model is more suitable for preliminary estimation and rapid simulation, but its prediction ability under high temperature, high pressure and high density is limited, so it should be used with caution.

6.2 Future work

Based on the results of this study, the following are recommendations for future work:

6.2.1 Peng-Robinson Model improvement

Future studies can improve the Peng-Robinson model, especially under high temperature and high pressure conditions, by introducing corrections to enhance the model's ability to describe non-ideal mixtures.

Combining the advantages of other equations of state to develop a hybrid model that enables it to provide more accurate specific heat capacity predictions over a wider range of conditions.

6.2.2 Model verification and experimental data support

Although the results of this study are based solely on model predictions, the accuracy of both models can be verified with experimental data in the future, especially for specific heat capacity measurements at high temperature, high pressure and high density. The experimental data will provide important reference for model improvement and calibration.

6.2.3 Further research on industrial applications

For industrial applications of ammonia-water absorption refrigeration systems, detailed process design and optimization can be performed using the Original Model to improve system efficiency and energy saving.

Peng-Robinson model can be used for rapid estimation in the early stages of process design, but should be further validated in practical applications with more accurate models to ensure the reliability and safety of the design.

6.2.4 Consider the influence of other thermal property parameters

This study focuses on specific heat capacity, but other thermophysical parameters (such as thermal conductivity,

viscosity, etc.) are equally important for the performance of ammonia-water absorption refrigeration systems. Future research can be extended to the modeling and prediction of other thermophysical parameters to fully optimize the performance of absorption refrigeration systems.

6.2.5 Application Scenario Expansion

In addition to absorption refrigeration systems, ammonia-water mixtures also have broad potential in other thermodynamic applications, such as heat pump systems and industrial cooling processes. In the future, the applicability and accuracy of the two models can be further evaluated for these applications, thus providing data support and optimization guidance for a wider range of industrial applications.

Through the above suggestions, the future work will help to further improve the accuracy of the model prediction and provide a more reliable and comprehensive scientific basis for the application of ammonia-water mixture in different thermodynamic systems.

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