SIMULATION RESEARCH ON ABSORPTION REFRIGERATION SYSTEM BASED ON NH_3-H_2O-LiBr VAPOR-LIQUID EQUILIBRIUM CALCULATION MODEL

by

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In order to investigate the NH_3+H_2O+LiBr (lithium bromide) absorption refrigeration cycle process and to simulate it accurately, a vapor-liquid equilibrium calculation model was proposed to obtain thermodynamic characteristic data of the ternary mixtures. The calculation of parameters of liquid phase is based on Wilson's equation and non-random two liquid equation. The vapor phase, assumed to consist of NH_3 and H_2O only, is described by The Redlich-Kwong Equation of State. The data of the equilibrium vapor pressure and the NH_3 concentration in liquid phase calculated by this model was compared with the experimental data, the difference is between 0.5% to 9.6% within the temperature range from 303 K to 425 K. The COP obtained by the simulation matches with that obtained by experiment and the absolute deviation is less than 0.02. Therefore, this calculation model can be used for simulation to extend the temperature range and pressure range of the system, so as to determine the design parameters of the absorption refrigeration system. The simulation results indicates that under different working conditions, the optimal generator temperature and concentration of adding LiBr can be selected, to which the theoretical explanations were given in this paper.

Key words: *absorption refrigeration system, solvation model, NH_3-H_2O-LiBr, vapor-liquid equilibrium*

Introduction

Energy consumption and environmental deterioration become concerns of individuals and governments more seriously due to the development of the whole world [1-4]. Currently, the traditional refrigeration technology mainly obtains the low temperature by the compressed steam refrigeration, which needs the extremely high mechanical energy input as the cost, and the irreversible loss of the system is relatively large.

Absorption refrigeration system and absorption heat pump system can obtain energy from low temperature heat source such as solar energy, geothermal energy, and industrial waste heat to improve the energy utilization efficiency and reduce the operation cost of system, so it is widely applied in the industry [5, 6]. Currently, NH_3+H_2O mixture is the common working pair of absorption refrigeration equipment and absorption heat pump. However, NH_3+H_2O absorption system requires much higher generator pressure, and due to the higher

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water vapor mass fraction of generator outlet, further rectification should be conducted, which will lead to the increase of system size, equipment cost and operation energy consumption [7]. Aimed at the problems existed in NH_3+H_2O absorption system, domestic and foreign scholars have put forward a kind of improved scheme, namely, add a third component to form ternary system in order to improve the disadvantages of binary system.

There are many options for adding a third component to the NH_3+H_2O system. The hydroxile in the solution will make the NH_3 ionization equilibrium move towards the direction of ion reduction [8], thus adding alkali into the NH_3+H_2O system can significantly reduce the concentration of NH_3 in the liquid phase at the vapor-liquid equilibrium [9-12]. Besides adding alkali, there are lots of researches of adding soluble salt in NH_3+H_2O solution. Taboas *et al.* [13] adopted NH_3-$LiNO_3$-H_2O as the operation working fluid, and found its performance coefficient higher than that of ammonia+water working pair. Moreover, the difference is more obvious at the lower temperatures. At the temperature of 85 °C, NH_3-$LiNO_3$-H_2O can obtain the low temperature of –17.5 °C and the outlet water content of the generator is less than 1.5%. Therefore, the rectifier can be eliminated and the generator can be applied in solar absorption refrigeration. Sathyabhama [14] measured the saturation parameters of NH_3-H_2O, NH_3-H_2O-$LiNO_3$ and NH_3-H_2O, NH_3-H_2O-LiBr mixtures. The results showed that the increase of salt could improve the mass transfer effect of NH_3+H_2O working pair.

Yuan *et al.* [15] studied the improvement effect of ternary working fluid by comparing the NH_3+H_2O absorption refrigeration system and NH_3+H_2O+LiBr absorption refrigeration system, and found that the size of the rectifier with ternary working fluid can be reduced about 16%, while the absorption pressure and generation pressure can be lower. Peters *et al.* [16, 17] studied vapor-liquid and solid-liquid phase equilibria of NH_3-H_2O-LiBr through experiments, and put forward a solvation model that can be used for phase equilibrium calculation. The model has very important significance for extending the range of temperature and pressure to simulate the operation of ternary absorption refrigeration system. So far there is no way to get the optimal design parameters of the ternary absorption refrigeration system by accurate simulation, which can only be determined by experiments.

In this paper, the formation of ion clusters is assumed, and the non-random two liquid (NRTL) equation is used to calculate the activity coefficients of the components and ion complexes in the solution [18]. The calculation model of vapor-liquid equilibrium data of the ternary system is obtained by iterative method, and is used to determine the input parameters of the rectifying tower during system simulation, the accuracy of which is verified by comparison with experimental data. The calculation model can be used to simulate the cycle process of the ternary absorption refrigeration systems more accurately, and thus can be used to extend the temperature range and pressure range of the system, to analyze the influencing factors of the system performance coefficient and to determine optimal design parameters of the system.

Phase equilibrium calculation model of the NH_3-H_2O-LiBr mixtures

Vapor phase model

The vapor-liquid phase equilibrium data in NH_3-H_2O-LiBr system can be calculated by establishing the basic equations of thermodynamic model. The main criterion for phase equilibrium is that the chemical potential of any component in each phase of mutual equilibrium formed by multiple components should be equal. On the basis, the working equation of calculating vapor-liquid equilibrium can be obtained:

$$\varphi_i y_i p = \gamma_i \varphi_{oi} x_i p_i^0 \exp \int_{p_i^0}^{p} \frac{v_{oi}}{\mathrm{R}T} \mathrm{d}p \tag{1}$$

For NH_3-H_2O-LiBr ternary system, the following assumptions are made: the vapor phase only consists of H_2O and NH_3, the Poynting factor (*i.e.*, exponential term) in the equation is negligible within the temperature and pressure considered, and according to Lewis and Randall's rule [19], the fugacity coefficient of H_2O above the NH_3-H_2O-LiBr mixture is equal to the value of pure water in its liquid state, and the fugacity coefficient of NH_3 is equal to the value of pure NH_3 in its liquid state.

Under these assumptions, eq. (1) can be simplified:

$$p_{\mathrm{H_2O}} = x_{\mathrm{H_2O}} \gamma_{\mathrm{H_2O}} p_{\mathrm{H_2O}}^0 (T) \tag{2}$$

$$p_{\mathrm{NH_3}} = x_{\mathrm{NH_3}} \gamma_{\mathrm{NH_3}} p_{\mathrm{NH_3}}^0 (T) \tag{3}$$

$$p = p_{\mathrm{H_2O}} + p_{\mathrm{NH_3}} \tag{4}$$

where $p_{\mathrm{H_2O}}$ is the partial pressure of water vapor and $p_{\mathrm{NH_3}}$ – the partial pressure of ammonia vapor. Besides, $p_{H_2O}^0(T)$ is the saturated vapor pressure of pure water at the temperature, T, and $p_{\mathrm{NH_3}}^0(T)$ is the saturated vapor pressure of pure ammonia at the temperature, T. The saturated vapor pressure of pure water and pure NH_3 at different temperature can be calculated by The Redlich-Kwong equation of state [20]

$$p_i^0(T) = \frac{\mathrm{R}T}{V_i - b} - \frac{a(T)}{V_i(V_i + b)} \tag{5}$$

$$a(T) = a_{\mathrm{c}} \alpha(T) \tag{6}$$

where $\alpha(T)$ is the temperature function equal to unity at the critical point and V_i – the molar volume of the pure substance i.

The coefficients b and a_c are determined using the critical parameters (T_c, P_c) of the pure substance, which is selected as T_c = 25 °C and P_c = 1 atm:

$$b = 0.08664 \frac{\mathrm{R}T_{\mathrm{c}}}{P_{\mathrm{c}}} \tag{7}$$

$$a_c = 0.42748 \frac{\mathrm{R}^2 T_{\mathrm{c}}{}^2}{P_{\mathrm{c}}} \tag{8}$$

The original expression of the temperature function $\alpha(T)$ is:

$$\alpha(T) = \frac{1}{\sqrt{T^r}} \tag{9}$$

$$T^r = T / T_c \tag{10}$$

Liquid phase model

Based on Stokes-Robinson's ion hydration theory [21], ion hydration may reduce the amount of solvent molecules and increase the volume of solute molecules, thus may change the activity coefficient of the electrolyte. The LiBr is partially ionized after dissolving in aqueous NH_3 solution, and the ionization forms Li^+ and Br^-, which are surrounded by ammonia and water molecules, can form ionic complexes. In the model, NH_3 and H_2O are both regarded as solvents and LiBr as solute. The schematic diagram of the ion hydration theory is shown in figs. 1 and 2. However, based on the local composition model proposed by Wilson [22], because the distribution of molecules in the solution is not uniform and the forces among the molecule pairs are not equal, the quasi-chemical equilibrium formula of forming ion clusters in the ternary liquid phase of NH_3-H_2O-LiBr proposed by Peters is put forward for modification [17]:

$$m\mathrm{H_2O} + \mathrm{LiBr} \rightleftarrows \mathrm{Li^+(H_2O)}_{m^+} + \mathrm{Br^-(H_2O)}_{m^-} \tag{11}$$

$$n\mathrm{NH_3} + \mathrm{LiBr} \rightleftarrows \mathrm{Li^+(NH_3)}_{n^+} + \mathrm{Br^-(NH_3)}_{n^-} \tag{12}$$

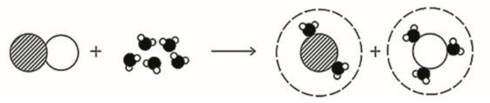

Figure 1. Interaction between lithium bromide and water molecules

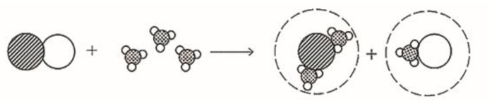

Figure 2. Interaction between lithium bromide and ammonia molecules

The parameters m, n, $m^\pm$, $n^\pm$ are called the solvation coefficient, and their relationship is:

$$m = m^+ + m^- \tag{13}$$

$$n = n^+ + n^- \tag{14}$$

A large amount of experimental evidences show m and n are mainly influenced by the initial concentration x^o_{LiBr} of LiBr in the solution before solvation [16, 23]. In a relatively wide range of temperature and concentration, the relationship between the solvation coefficient and the phase equilibrium experimental data can be obtained by fitting and analyzing a large number of VLE experimental data:

$$m + n = 4 - 5x^o_{\mathrm{LiBr}} \tag{15}$$

$$\frac{n^+}{m^+} = a^+ \frac{x^o_{\mathrm{NH_3}}}{x^o_{\mathrm{H_2O}}} x^o_{\mathrm{LiBr}} \tag{16}$$

$$\frac{n^-}{m^-} = a^- \frac{x^o_{\mathrm{NH_3}}}{x^o_{\mathrm{H_2O}}} x^o_{\mathrm{LiBr}} \tag{17}$$

$$\frac{n^+ + m^+}{n^- + m^-} = \hat{a} \tag{18}$$

where *m* is the solvation coefficient between LiBr and H_2O, *n* – the solvation coefficient between LiBr and NH_3, $x_{NH_3}^o$, $x_{H_2O}^o$, x_{LiBr}^o represent the initial mole fraction of NH_3, H_2O, and LiBr before solvation respectively, $\hat{a}$ – a fixed constant, a^+ and a^- – the parameters related to temperature, calculate based on the following formula:

$$a^+ = a_0^+ \exp\frac{-a_e^+}{\mathrm{R}T} \tag{19}$$

$$a^- = a_0^- \exp\frac{-a_e^-}{\mathrm{R}T} \tag{20}$$

Thereinto, $a_0^\pm$ and $a_e^\pm$ are the optimization parameters of the solvation model. Table 1 shows the values of each parameter [17].

Table 1. Solvation parameters

a_0^+	a_0^-	$\hat{a}$	a_e^+ [Jmol^{-1}]	a_e^- [Jmol^{-1}]
0.1212	1	1	291	14375

The model also includes the association reaction of NH_3 and H_2O molecules forming the second complex [17]. The correlative quasi-chemical reaction is:

$$\mathrm{NH_3 + H_2O \rightleftharpoons (NH_3)(H_2O)} \tag{21}$$

The NRTL equation was put forward by Renon and Prausnitz in 1968 [24]. The NRTL equation can be applied to partial miscibility and complete miscibility system [25]. The expression of excess free enthalpy of solution for NRTL equation is:

$$\frac{G^E}{\mathrm{R}T} = \sum_i \left[x_i \frac{\sum_j (\tau_{ji} G_{ji} x_j)}{\sum_k (G_{ki} x_k)} \right] \tag{22}$$

Thus, the activity coefficient equation can be obtained:

$$\ln \gamma_i = \frac{\sum_j (\tau_{ji} G_{ji} x_j)}{\sum_k (G_{ki} x_k)} + \sum_j \frac{G_{ij} x_j}{G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_i (\tau_{ij} G_{ij} x_i)}{\sum_k (G_{kj} x_k)} \right] \tag{23}$$

$$\tau_{ji} = \frac{g_{ji} - g_{jj}}{\mathrm{R}T} \tag{24}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{25}$$

The parameters of NRTL activity coefficient equation are shown in tabs. 2 and 3. Here α_{jj} is the NRTL's interaction parameter and g_{jj} – the molecular energy between molecules of species *j* and *i*.

The $C^\pm$ represents the ionic complexes $Li^+(H_2O)_{m^+}$ and $Br^-(H_2O)_{m^-}$, $Z^\pm$ represents the ionic complexes $Li^+(NH_3)_{n^+}$ and $Br^-(NH_3)_{n^-}$, A represents ammonia monohydrate $(NH_3)(H_2O)$.

Table 2. Parameter α_{ji} of NRTL activity coefficient equation

j/*i*	H_2O	LiBr	$C^\pm$	NH_3	A	$Z^\pm$
H_2O	0	0.651	0.170	0.126	0.006	0.001
LiBr	0.651	0	0	0.819	0.003	0
$C^\pm$	0.170	0	0	0.041	0.036	0
NH_3	0.126	0.819	0.041	0	5.626	0
A	0.006	0.003	0.036	5.626	0	1.883
$Z^\pm$	0.001	0	0	0	1.883	0

Table 3. Parameter g_{ji} of NRTL activity coefficient equation

j/*i*	H_2O	LiBr	$C^\pm$	NH_3	A	$Z^\pm$
H_2O	0	–13728	–6206	–5029	–17358	–22979
LiBr	–6878	0	0	51081	-49	0
$C^\pm$	644	0	0	4579	46450	0
NH_3	30516	79785	33274	0	1750	–26826
A	16295	26754	73252	–142	0	37119
$Z^\pm$	–16128	0	0	–55521	10317	0

The equilibrium constants of the quasi-chemical equilibrium eqs. (5) and (6) of solvation in the ternary mixed solution of NH_3-H_2O-LiBr and the associated reaction eq. (15) of ammonia and water molecules are, respectively:

$$K_C = \frac{(\gamma_{C^\pm} x_C)^2}{(\gamma_{\mathrm{H_2O}} x_{\mathrm{H_2O}})^m (\gamma_{\mathrm{LiBr}} x_{\mathrm{LiBr}})} \tag{26}$$

$$K_Z = \frac{(\gamma_{\mathrm{Z}^\pm} x_{\mathrm{Z}})^2}{(\gamma_{\mathrm{NH_3}} x_{\mathrm{NH_3}})^n (\gamma_{\mathrm{LiBr}} x_{\mathrm{LiBr}})} \tag{27}$$

$$K_A = \frac{\gamma_{\mathrm{A}} x_{\mathrm{A}}}{(\gamma_{\mathrm{H_2O}} x_{\mathrm{H_2O}})(\gamma_{\mathrm{NH_3}} x_{\mathrm{NH_3}})} \tag{28}$$

The values of these equilibrium constants are relevant with the temperature. The Van't Hoff equation can be used to represent its correlation with temperature:

$$K_i = K_i^o \exp\frac{-\Delta H_i^o}{\mathrm{R}T} \tag{29}$$

The parameter values of $\mathrm{LiBr} + \mathrm{H_2O}$, $\mathrm{LiBr} + \mathrm{NH_3}$, and $\mathrm{NH_3} + \mathrm{H_2O}$ in each reaction equilibrium constant formula are shown in tab. 4 [17].

Table 4. Equilibrium constant K_i^o and standard enthalpy change ΔH_i^o parameters in standard state of each reaction

Equilibrium reaction	Equilibrium equation	$\ln K_i^o$	ΔH_i^o [Jmol^{-1}]
C (LiBr + H_2O solvation)	(5)	–5.7953	–49651.14
Z (LiBr + NH_3 solvation)	(6)	–0.3143	–5728.00
A (NH_3 + H_2O associated reaction)	(15)	–3.8196	–13359.92

During the formation of ionic clusters by solvation in the NH_3-H_2O-LiBr ternary mixed solution, the initial molar fractions of NH_3, H_2O, LiBr in the solution changed. The x_{NH_3}, x_{H_2O}, and x_{LiBr} represent the molar fractions of NH_3, H_2O, and LiBr in the solution after salvation, respectively. Meanwhile, since the solution is always in an electrically neutral state, which is an objective law, the mole fraction of positive and negative ion clusters generated by solvation should be equal:

$$x_{\mathrm{Li^+(H_2O)}_{m^+}} = x_{\mathrm{Br^-(H_2O)}_{m^-}} = x_\mathrm{C} \tag{30}$$

$$x_{\mathrm{Li^+(NH_3)}_{n^+}} = x_{\mathrm{Br^-(NH_3)}_{n^-}} = x_\mathrm{Z} \tag{31}$$

Considering the associated reaction between NH_3 and H_2O, the following relation can be obtained based on the quantity balance equation of substances:

$$x_\mathrm{H_2O} = x_\mathrm{H_2O}^o[1+(m-1)x_\mathrm{C} + (n-1)x_\mathrm{Z}] - mx_\mathrm{C} + x_\mathrm{A}(x_\mathrm{H_2O}^o - 1) \tag{32}$$

$$x_\mathrm{NH_3} = x_\mathrm{NH_3}^o[1+(m-1)x_\mathrm{C} + (n-1)x_\mathrm{Z}] - nx_\mathrm{Z} + x_\mathrm{A}(x_\mathrm{NH_3}^o - 1) \tag{33}$$

$$x_\mathrm{LiBr} = x_\mathrm{LiBr}^o[1+(m-1)x_\mathrm{C} + (n-1)x_\mathrm{Z}] - x_\mathrm{C} - x_\mathrm{Z} + x_\mathrm{A} x_\mathrm{LiBr}^o \tag{34}$$

$$x_\mathrm{NH_3} + x_\mathrm{H_2O} + x_\mathrm{LiBr} + 2x_\mathrm{C} + 2x_\mathrm{Z} + x_\mathrm{A} = 1 \tag{35}$$

Calculation model

For the ternary mixed solution of NH_3-H_2O-LiBr, the three species were mixed in a certain ratio at the beginning. Before solvation occurs and the vapor-liquid equilibrium is formed, according to the initial mixing ratio the initial mole fractions $x_\mathrm{NH_3}^o$, $x_\mathrm{H_2O}^o$, x_LiBr^o of NH_3, H_2O, and LiBr in liquid phase and the temperature, *T*, are known, to calculate the concentration of each particle in the solution after solvation, the iterative process will next be explained.

Firstly, select the appropriate $x_\mathrm{H_2O}$ and $x_\mathrm{NH_3}$ from the allowed range that meet the following conditions:

$$0 < x_\mathrm{H_2O} \le x_\mathrm{H_2O}^o \tag{36}$$

$$0 < x_\mathrm{NH_3} \le x_\mathrm{NH_3}^o \tag{37}$$

The solvation coefficients *m* and *n* can be obtained from the empirical formulas eqs. (13)-(20), and combined with the assumed $x_\mathrm{H_2O}$ and $x_\mathrm{NH_3}$, the molar fractions of various components in the solution after solvation can be calculated by the quantity balance equation of substances eqs. (32)-(35). Then, according to eqs. (23)-(25), the activity coefficients of various components in the solution can be calculated. Under the condition of certain temperatures, it can be speculated from the Van't Hoff equation that the equilibrium constant K_C of the solvation reaction between LiBr and H_2O, the equilibrium constant K_Z of the solvation reaction between LiBr and NH_3 as well as the equilibrium constant K_A of associated reaction between NH_3 and H_2O are respectively fixed values. Combining eq. (26)-(28), the following functional relationship can be obtained:

$$f(K_C, x_{NH_3}, x_{H_2O}) = K_C - \frac{(\gamma_{C^\pm} x_C)^2}{(\gamma_{H_2O} x_{H_2O})^m (\gamma_{LiBr} x_{LiBr})} = 0 \tag{38}$$

$$f(K_Z, x_{NH_3}, x_{H_2O}) = K_Z - \frac{(\gamma_{Z^\pm} x_Z)^2}{(\gamma_{NH_3} x_{NH_3})^n (\gamma_{LiBr} x_{LiBr})} = 0 \tag{39}$$

$$f(K_A, x_{NH_3}, x_{H_2O}) = K_A - \frac{\gamma_A x_A}{(\gamma_{H_2O} x_{H_2O})(\gamma_{NH_3} x_{NH_3})} = 0 \tag{40}$$

Thus, the iterative re0lation about x_{H_2O} and x_{NH_3} can be obtained, which can be used to check whether the selected x_{H_2O} and x_{NH_3} meet the thermodynamic conditions. The iterative method can be used to determine whether the selected mole fraction can make the eqs. (38)-(40) be established.

Validation of calculation model

Calculated vapor pressure in equilibrium state

The model can be used to calculate the vapor pressure at the vapor-liquid equilibrium state of the ternary working fluid under certain temperature and certain concentration of NH_3 and salt in the solution. Figures 3 and 4 show the comparison of the calculated results of the calculation model described in this paper with the experimental data. When the temperature is 303 K and the initial salt mass fraction is 50%, the calculated vapor pressure data obtained by the calculation model have a minimum error of 0.5% and a maximum error of 7.8% with the experimental data published by Peters [16]. When the temperature is 375 K and the initial salt mass fraction is 20%, the calculated vapor pressure data obtained by the calculation model have a minimum error of 0.6% and a maximum error of 9.1% with the experimental data published by Peters [16].

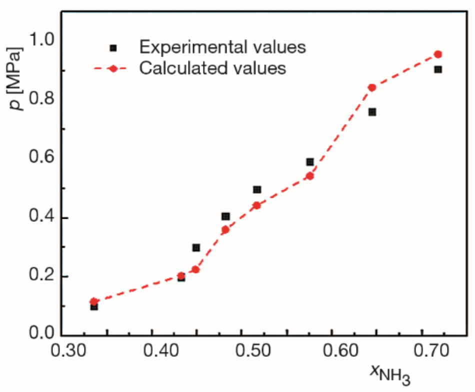

Figure 3. Comparison of data when the temperature is 303 K, the initial salt mass fraction is 50%

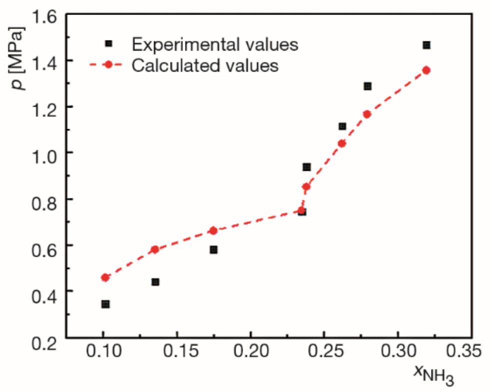

Figure 4. Comparison of data when the temperature is 375 K, the initial salt mass fraction is 20%

Calculated concentration of NH_3 in equilibrium state

The model can also be used to calculate the NH_3 concentration at the vapor-liquid equilibrium state of the ternary working fluid under certain temperature, certain vapor pressure and certain concentration of salt in the solution. Figures 5 and 6 show the comparison of the calculated results of the calculation model described in this paper with the experimental data. When the temperature is 333 K and the initial salt mass fraction is 30%, the calculated liquid-phase NH_3 concentration data obtained by the calculation model have a minimum error of 2.1% and a maximum error of 9.6% with the experimental data published by Peters [16]. When the temperature is 475 K and the initial salt mass fraction is 28%, the calculated liquid-phase NH_3 concentration data obtained by the calculation model have a minimum error of 1.4% and a maximum error of 8.4% with the experimental data published by Peters [16].

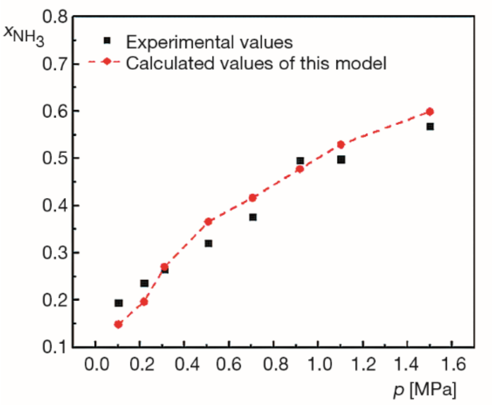

Figure 5. Comparison of data when the temperature is 333K, the initial salt mass fraction is 30%

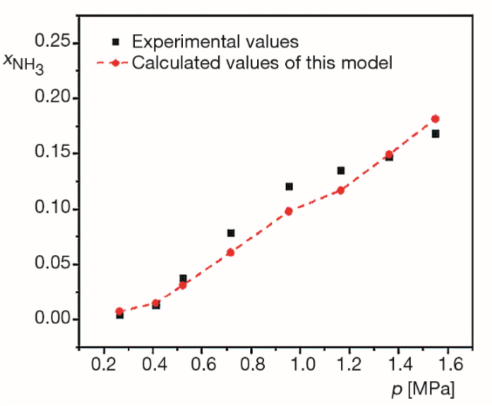

Figure 6. Comparison of data when the temperature is 425 K, the initial salt mass fraction is 28%

Therefore, the calculation results of the model based on the solvation model and NRTL equation described in this paper are very accurate, which match the experimental data well.

Description of ternary absorption refrigeration system model

The system diagram of the cycle established by ASPEN PLUS software is shown in fig. 7. In this figure, module 1 represents the rectifying tower, including the generator, stripping section, distillation section and reflux condenser. The NH_3 concentration of the tower bottom was determined by the calculation model according to the temperature of the tower bottom, and then the produced quantity of the NH_3 vapor of the tower top was calculated based on the conservation of mass. Module 2 represents the condenser. Module 3 represents the subcooler. Module 4 represents the evaporator. All of the NH_3 is assumed to be evaporated, and the evaporator temperature, T_0, is set as –10 °C~15 °C. Module 5 represents the absorber. Module 6-1 and 6-2 represent valves. Module 7 represents the heat exchanger. Module 8 represents the solution pump. The process of refrigeration is as follows: the steam produced from the top of the rectifying tower is relatively pure NH_3, the NH_3 enters the condenser to be condensed, and the heat of condensation is taken away by the cooling water. The condensed

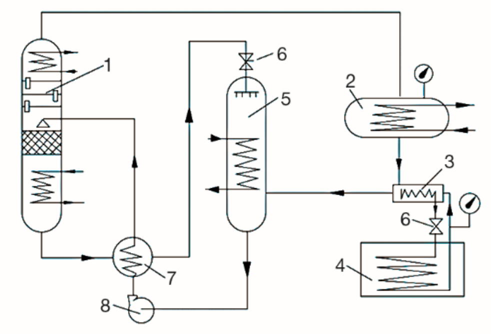

Figure 7. The NH_3-H_2O-LiBr absorption refrigeration system

liquid NH_3 has a heat exchange with the NH_3 vapor from the evaporator in the subcooler, and then the liquid NH_3 becomes supercooled liquid. It is throttled by the valve to form wet vapor and then enters the evaporator to evaporate. The refrigeration effect is conducted in the evaporator. After evaporating, the NH_3 vapor is heated in the supercooler, and then is absorbed by the dilute solution in the absorber. The unsaturated dilute solution comes from the rectifying tower, which is cooled by the concentrated solution from the absorber in the heat exchanger, and then decompressed by the valve. The dilute solution absorbs the NH_3 vapor and becomes the concentrated solution, which is boosted by the solution pump, and heated by the heat exchanger, and then enters the rectifying tower for generation and rectification. Pure NH_3 is obtained in the rectifying tower. The system cycle continues in this way.

The concentration of NH_3 in the concentrated solution which comes from the absorber (5) is $x'_{\mathrm{NH_3}}$, and the concentration of NH_3 in the dilute solution which comes from the rectifying tower (1) is $x''_{\mathrm{NH_3}}$, then the deflation range Δx is:

$$\Delta x = x'_{\mathrm{NH_3}} - x''_{\mathrm{NH_3}} \tag{41}$$

The heat load of generator at 1 is Q_{gen}, and the refrigerating capacity of the evaporator at 4 is Q_0, then the COP of system is:

$$\mathrm{COP} = \frac{Q_0}{Q_{\mathrm{gen}}} \tag{42}$$

Because the phase equilibrium physical property data of the NH_3+H_2O+LiBr ternary working fluid can be accurately obtained by the calculation model put forward in this paper, thereby the input parameters of the rectifying tower can be accurately determined. As a result it can be very accurate to simulate the process of NH_3-H_2O-LiBr ternary absorption refrigeration cycle to obtain the analysis of the influence factors in the performance of system.

Results and discussion

Mechanism of action of LiBr

Figure 8 shows the molar fraction relationship of the three kinds of particles of LiBr, H_2O and ionic complex $C^{\pm}$ in liquid phase when the ionic complex is formed by LiBr and solvent of water under the conditions of 303 K and 333 K for the temperature, respectively, and the initial LiBr mass fraction of 34%. Figure 9 shows the molar fraction relationship of the three kinds of particles of LiBr, NH_3 and ionic complex $Z^{\pm}$ in liquid phase when the ionic complex is formed by LiBr and solvent of NH_3 under the conditions of 303 K and 333 K for the temperature, respectively, and the initial LiBr mass fraction of 34%. Compared the two figures, it can be speculated that under a certain temperature, both H_2O and NH_3 can solvate LiBr, while the solvation effect of H_2O is stronger than that of NH_3. In the solution, the proportion of ion complex formed by LiBr and H_2O is more than that formed by LiBr and NH_3. Therefore, compared with NH_3-H_2O binary solution, the addition of LiBr can effectively reduce the amount of evaporation of water from the solution, and then can reduce the distillation loss and increase the COP of the system. However, for the absorber, adding too much LiBr will cause difficulty in the absorption process, which is not conducive to the operation of the entire system. Thus the optimal LiBr concentration to be added to the absorption system should be determined by simulation.

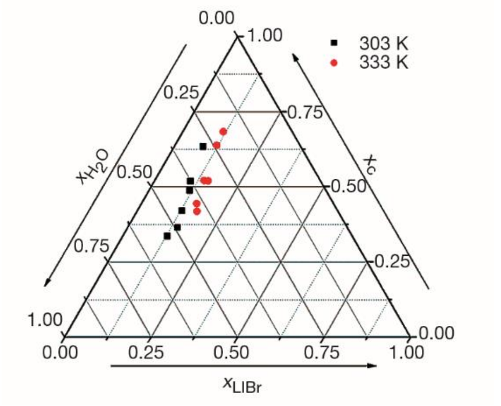

Figure 8. Mole fraction of LiBr, H_2O, and $C^\pm$

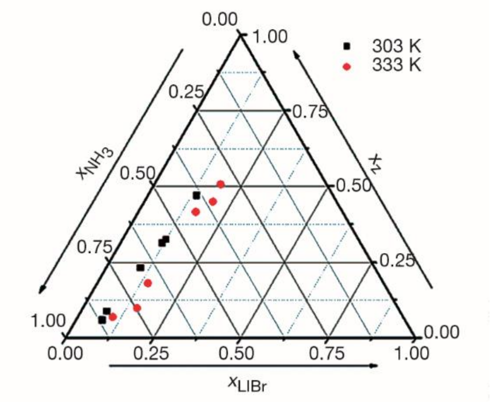

Figure 9. Mole fraction of LiBr, NH_3, and $Z^\pm$

Comparison of experimental results and simulation results

By setting the experimental conditions, recording the corresponding data and calculating the COP of the system, some experimental results are obtained and shown in tab. 5.

Table 5. Some experimental conditions and corresponding results

ω_{LiBr}	T_0 [°C]	T_C [°C]	T_{gen} [°C]	Q_0 [W]	Q_{gen} [W]	COP
5%	–10	28	100	861.88	2419.23	0.3563
5%	–13	28	110	1685.14	4053.38	0.4157
5%	–10	25	110	1837.82	4318.15	0.4256
5%	–10	28	110	1438.00	3742.51	0.3842
5%	–10	34	110	775.19	2561.57	0.3062
5%	–7	28	110	1138.94	3418.52	0.3332
5%	–10	28	120	1934.85	4669.07	0.4144
15%	–10	28	100	645.55	1767.59	0.3652
15%	–13	28	110	1422.15	3227.91	0.4406
15%	–10	25	110	1491.75	3415.21	0.4368
15%	–10	28	110	1208.41	3015.46	0.4007
15%	–10	34	110	670.74	2052.39	0.3268
15%	–7	28	110	946.70	2676.41	0.3537
15%	–10	28	120	1667.82	3788.41	0.4402

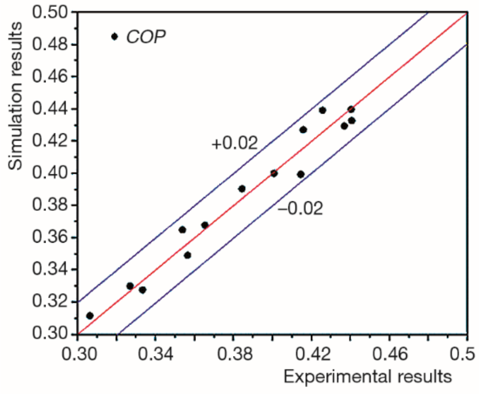

Figure 10. Absolute deviation between experimental results and simulation results

Figure 10 represents the absolute deviation between the results obtained by experimental measurement [26] and the results obtained by simulation using the calculation model proposed in this paper. According to fig. 10, it can be inferred that the absolute deviation is less than 0.02.

Influence of generator temperature, on system performance

The influence of generator temperature of ternary working fluid absorption refrigeration system on COP is shown in fig. 11. Input parameters are: condenser temperature T_C = 20 °C, evaporator temperature T_C = –10 °C, and LiBr mass fraction ω_{LiBr} are 0%, 5%, 10%, and 15%, respectively. According to fig. 11, the COP of system increases with the increase of generator temperature, but the curve of growth tends to be flat. The reason is that the increase of generator temperature is conducive to the generating process, which will cause the NH_3 concentration in the solution to decrease after the generating process, so the concentration of NH_3 in the vapor from the top of rectifying tower will increase, which will lead to the increase of the deflation range and the decrease of cycle rate, thus, the COP of system will increase. But as the generator temperature continues increasing and with the solvation of LiBr and water in the solution, the trend of decrease of the NH_3 concentration in the solution gradually slows down, but the heat consumption of the rectifier continues to increase. As a result, the curve of growth tends to be flat.

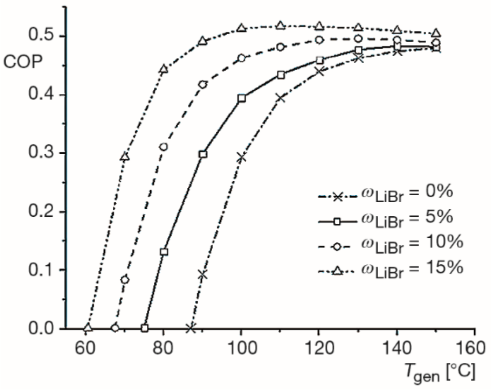

Figure 11. The COP varies with T_{gen}

It can be inferred from fig. 11 that when the condenser temperature is equal to 20 °C and the evaporator temperature is equal to –10 °C, for different LiBr concentrations, the system has different optimal generator temperatures. When the mass fraction of LiBr ω_{LiBr} = 0%, the optimal temperature of the absorption refrigeration system is 150 °C. When the mass fraction of LiBr ω_{LiBr} = 5%, the optimal temperature of the absorption refrigeration system is 140 °C. When the mass fraction of LiBr ω_{LiBr} = 10%, the optimal temperature of the absorption refrigeration system is 120 °C. When the mass fraction of LiBr ω_{LiBr} = 15%, the optimal temperature of the absorption refrigeration system is 110 °C. It indicates that for different working conditions, the system has a certain optimal generator temperature.

Influence of lithium bromide concentration on system performance

In fig. 12, the input parameters are: when condenser temperature T_C = 25 °C, evaporator temperature T_0 = – 10 °C, generator temperature T_{gen} = 100 °C, the change relationship of NH_3 concentration, x'_{NH_3}, of the effluent concentrated solution from the absorber, NH_3 concentration, x''_{NH_3}, of the effluent dilute solution from the generator at the bottom of rectifying tower and deflation range Δx with LiBr mass fraction, ω_{LiBr}. It can be seen from the figure that the concentration of NH_3, x'_{NH_3}, of concentrated solution and that of x''_{NH_3} of dilute solution decreases with the increase of LiBr concentration. When $\omega_{LiBr} \leq 0.075$, the concentration of NH_3 in concentrated solution has a small decrease trend, and that in dilute solution has a large decrease trend. When $0.075 < \omega_{LiBr} < 0.16$, the trend of NH_3 concentration in concentrated solution is still small, while that in dilute solution tends to be flat. When $\omega_{LiBr} \geq 0.16$, the decrease trend of NH_3 concentration in the concentrated solution suddenly becomes big, while the decrease trend of NH_3 concentration in the dilute solution remains flat. It led to the deflation range Δx increasing firstly and then decreasing with the LiBr concentration ω_{LiBr} increasing and reaching the maximum when ω_{LiBr} is equal to 0.16. Since under the certain temperature, the solvation of LiBr and H_2O is significantly stronger than that of LiBr and NH_3, namely, LiBr has a stronger ability of combining H_2O molecules than that of combining NH_3 molecules. Thus, with the increase of LiBr concentration, the heat of rectification will always decrease, but the absorption process will be influenced by the increase of LiBr concentration, so the deflation range will first increase then decrease, in general, the COP of system is also manifested as first increase and then decrease.

The influence of LiBr concentration on COP in ternary working fluid absorption refrigeration system is shown in fig. 13. Input parameters are: condenser temperature T_C = 25 °C, generator temperature T_{gen} = 100 °C, and evaporator temperature T_0 are, respectively, –10 °C, –5 °C, and 0 °C. With the increase of LiBr concentration ω_{LiBr}, COP first increased and then decreased, which means each independent system with different working conditions corresponds to an optimal LiBr mass fraction. Compared with the solid black line in fig. 12, it can be found that when the deflation range is at maximum, the COP is at maximum.

From fig. 13, when the condenser temperature T_C = 25 °C, the generator temperature T_{gen} = 100 °C, and the evaporator temperature T_0 = – 10 °C, the optimal mass fraction of LiBr for the system is ω_{LiBr} = 0.16. When the condenser temperature T_C = 25 °C, the generator

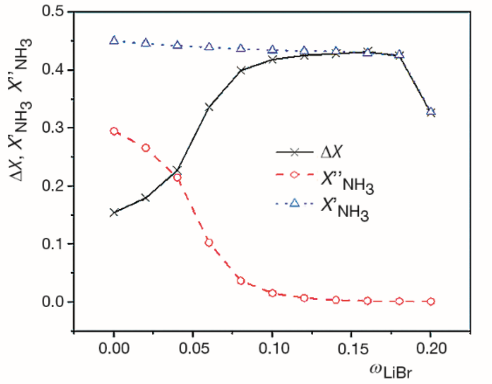

Figure 12. The x'_{NH_3}, x''_{NH_3} and Δx vary with ω_{LiBr}

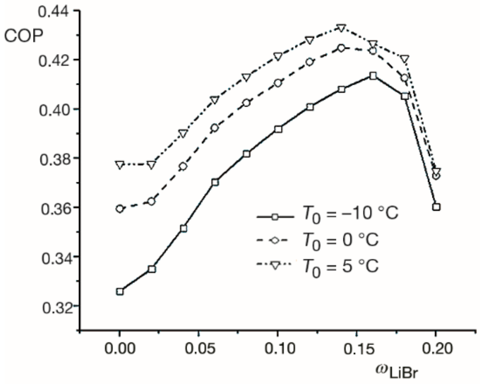

Figure 13. The COP varies with ω_{LiBr}

temperature T_{gen} = 100 °C, and the evaporator temperature T_0 = 0 °C, the optimal mass fraction of LiBr for the system is $\omega_{\mathrm{LiBr}} = 0.14$. When the condenser temperature T_{C} = 25 °C, the generator temperature T_{gen} = 100 °C, the evaporator temperature T_0 = 5 °C, the optimal mass fraction of LiBr for the system is $\omega_{\mathrm{LiBr}} = 0.14$.

Conclusions

In this paper, a vapor-liquid equilibrium calculation model was proposed to obtain thermodynamic characteristic data of the NH_3+H_2O+LiBr ternary mixtures based on NRTL equation and the solvation model put forward by Peters [17]. The calculation model is obtained by iterative method, and is used to determine the input parameters of the rectifying tower during system simulation, the accuracy of which is verified by the comparison with experimental data.

- The calculated equilibrium vapor pressure and the calculated NH_3 concentration in liquid phase based on the calculation model in this paper match with experimental data published by Peters [16], the difference is between 0.5% to 9.6% within the temperature range from 303 K to 425 K.
- Under a certain temperature, both H_2O and NH_3 can solvate LiBr, while the solvation effect of H_2O is stronger than that of NH_3. In the solution, the proportion of ion complex formed by LiBr and H_2O is more than that formed by LiBr and NH_3. Therefore, compared with NH_3-H_2O binary solution, the addition of LiBr can effectively reduce the amount of evaporation of water from the solution, and then can reduce the distillation loss and improve the coefficient of the system. However, for the absorber, adding too much LiBr will cause difficulty in the absorption process, which is not conducive to the operation of the entire system. Thus the optimal LiBr concentration to be added to the absorption system should be determined by simulation.
- The COP obtained by the simulation matches with that obtained by experiment and the absolute deviation is less than 0.02. Therefore, this calculation model can be used for simulation to extend the temperature range and pressure range of the system, so as to determine the design parameters of the absorption refrigeration system. The simulation results indicates that under different working conditions, the optimal generator temperature and concentration of adding LiBr can be selected. For example, when the condenser temperature T_{C} = 25 °C, the generator temperature T_{gen} = 100 °C, and the evaporator temperature T_0 = –10 °C, the optimal mass fraction of LiBr for the system is 16%.

Nomenclature

A – association
C – solvation (LiBr + H_2O)
g_{ji} – molecular energy between molecules of species *j* and *i*
ΔH_i^o – heat of activation
K_i – equilibrium constant
K_i^o – equilibrium constant in the standard state
m – solvation coefficient (LiBr + H_2O)
n – solvation coefficient (LiBr + NH_3)
p – pressure
p_i^0 – vapor pressure of pure species *i*
Q_0 – refrigerating capacity of the evaporator
Q_{gen} – heat load of generator
R – gas constant
T – temperature
T_0 – evaporator temperature
T_{C} – condenser temperature
T_{gen} – generator temperature
x_i – mole fraction of species *i* in the liquid phase
x_i^0 – initial mole fraction of species *i* in the solution before solvation
y_i – mole fraction of species *i* in the vapor phase
Z – solvation (LiBr + NH_3)
v_{oi} – molar volume of pure species *i*

Greek symbols

α_{ji} – NRTL’s interaction parameter
γ_i – activity coefficient of species *i*

φ_i – fugacity coefficient of species *i*
φ_{oi} – fugacity coefficient of pure species *i*
ω_{LiBr} – mass fraction of lithium bromide

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