

Theoretical Formulation of the Thermodynamic Properties of Ammonia-Water and Ammonia-Water-Lithium Bromide Solutions

Suhas B.G, Kavadiki Veerabhadrapa



Abstract: System of Ammonia-Water-Lithium Bromide overcomes the disadvantage of Ammonia-Water absorption refrigeration system. Addition of lithium bromide reduces the formation of water vapour thus presents its entry into the condenser. A set of computational formulations of thermodynamic and Thermophysical properties of Ammonia-Water, Water-Lithium bromide and Ammonia-Water-Lithium Bromide solutions at different pressures and temperatures are presented in the paper. Obtained results are validated with the experimental data which were available in the literature. It is found to be in good agreement with those values of the literature..

Keywords: Ammonia water, Binary mixture, Lithium bromide, Ternary mixture

I. INTRODUCTION

The binary mixtures of Ammonia-Water (NH₃-H₂O) and Water-Lithium Bromide (LiBr) are working substances applied both in absorption heat pump and refrigeration system. The disadvantage of LiBr binary mixture came from its pressure below the atmosphere. The NH₃-H₂O binary mixture in the system has high water content in the vapour phase, resulting in an expensive dephlegmator in the vapour absorption refrigeration system. This leads to high vapour pressure at elevated temperatures [1]. The strong ability of absorbing water by LiBr in Lithium Bromide (NH₃-H₂O-LiBr) system results in the lower vapour content of the system [2,3]. Thermodynamic modelling is important in the field of vapour absorption cooling system [4,5,6]. Arun et al. [7] carried out a thermodynamic study on the performance of a series flow-type double-effect water-LiBr absorption chiller.

Xu and Dai [8] presented a similar analysis on performance of a parallel flow double effect water-LiBr absorption chiller. The current study highlights a methodological proposal for the thermodynamic calculation of a NH₃-H₂O-LiBr solution adopting the reference environment proposed by Yuyuan Wu et al.

[9] considering their physical and chemical components. This methodology represents to permit the expansion of control volume in cogeneration systems. Considering the necessity of a new description for the solutions over working ranges, the present study provides the values of enthalpy and entropy of NH₃-H₂O and NH₃-H₂O-LiBr in the different concentration and temperature range.

II. METHODOLOGY

Thermodynamic description of binary/ternary solutions requires an ideal fluid as a reference fluid. This is due to solute species because the pure solute is a solid substance in the standard state. The properties of this fluid are extrapolated from the partial molar properties where there is no mutual interaction between the ions in the mixture [10]. An osmotic coefficient is a quantity which characterizes the deviation of a solvent from ideal behavior. It is the way of expressing chemical composition of mixtures. Osmotic potential is determined by equation (1). Binary and Ternary mixture enthalpy and entropy are calculations are given in Equation (1)-(21)

$$\phi = 1 + \left[A + \left(\frac{G}{4} \right) m^{0.5} \right] + B + \left(\frac{H}{2} \right) m^{0.5} + C m^{1.5} + D m^2 + E m^{2.5} + F m^3 \tag{1}$$

Where m is mass fraction of solute having low boiling point.

$$A = a_{10} + \frac{a_{11}}{T} + \frac{a_{12}}{T^2} \tag{2}$$

$$B = a_{20} + \frac{a_{21}}{T} + \frac{a_{22}}{T^2} \tag{3}$$

$$C = a_{30} + \frac{a_{31}}{T} + \frac{a_{32}}{T^2} \tag{4}$$

$$D = a_{40} + \frac{a_{41}}{T} + \frac{a_{42}}{T^2} \tag{5}$$

$$E = a_{50} + \frac{a_{51}}{T} + \frac{a_{52}}{T^2} \tag{6}$$

$$F = a_{60} + \frac{a_{61}}{T} + \frac{a_{62}}{T^2} \tag{7}$$

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$$G = b_{10} + \frac{b_{11}}{T} + \frac{b_{12}}{T^2} \quad (8)$$

$$H = b_{20} + \frac{a_{21}}{T} + \frac{a_{22}}{T^2} \quad (9)$$

$$P = \ln(1.322\phi) \quad (10)$$

$$\phi = \alpha_1 - \beta_1 \ln(1.322\phi) \quad (11)$$

Where $\alpha_1 = 3.994$, $\beta_1 = 0.4535$

$$\eta = \exp(36\phi\beta m) \quad (12)$$

$$\theta = \eta \cosh(\phi) \quad (13)$$

$$p = \exp\left[\frac{\alpha - \ln(2\theta)}{B}\right] \quad (14)$$

$$v = 8314T \left[c_0 + \frac{c_1}{T} + \frac{c_2}{T^2} \right] \quad (15)$$

$$h_1 = \left(v_1 - T_1 \frac{dv}{dT} \right) (2.032 - p) \quad (16)$$

$$h_2 = \left(v_2 - T_2 \frac{dv}{dT} \right) (2.032 - p) \quad (17)$$

Enthalpy in binary and ternary mixture is calculated by using Equation (18), (19) and (20).

$$h_{bm,wa} = m_w h_w + m_a h_a \quad (18)$$

$$h_{bm,wlibr} = m_w h_w + m_{libr} h_{libr} \quad (19)$$

$$h_{tm,walibr} = m_{w+a} h_{w+a} + m_{w+a+libr} h_{w+a+libr} \quad (20)$$

Entropy of the Binary and Ternary mixture can be calculated by Equation (21). Constant values determined are given in Table.

$$s = \frac{(x c_1 T + x^2 c_2 T + x^3 c_3 T)}{(1 - 0.96x)} \ln(\phi) \quad (21)$$

x is mole fraction.

III. RESULTS AND DISCUSSIONS

The theoretical work is carried out to determine the enthalpy and entropy of ammonia-water, lithium bromide-water and lithium bromide-water-ammonia mixtures in liquid and vapour phases at different temperatures, pressures and mass fractions. Fig.1 shows the validation of pressure variation with different temperatures of lithium bromide-water mixture. The theoretical results are compared with that of experimental results of Yuyuan et al [9]. It can be seen that the predicted values of the pressure deviated about 15% from those values of the literature.

The Fig.2 shows that liquid enthalpy decreases with increase in liquid mass fraction of ammonia. As the pressure increases from 1 bar to 12 bar liquid mixture enthalpy increases. The ammonia added to water, causes the liberation of energy, which means it is an exothermic reaction. It deviates from Raoult's law of partial pressure causing decrease in enthalpy. This increases saturation point. The OH radical of water is attracted by NH_4^+ . But the attractive force of NH_4^+ to absorb OH of water decreases at lower pressure. As the pressure is reduced, the water becomes more susceptible to become vapour. Therefore, at higher pressure enthalpy increases due to presence of more NH_4^+ in the water.

The Fig. 3 shows that the vapour mixture enthalpy increases with increase in ammonia mass fraction and

pressures. The water vapour formed is very less, when the ammonia mass fraction is increased. So in order to form vapour more heat is to be supplied. Therefore the mixture vapour enthalpy increases and the vapour formation reduces at higher pressures, due to elevation in saturation point

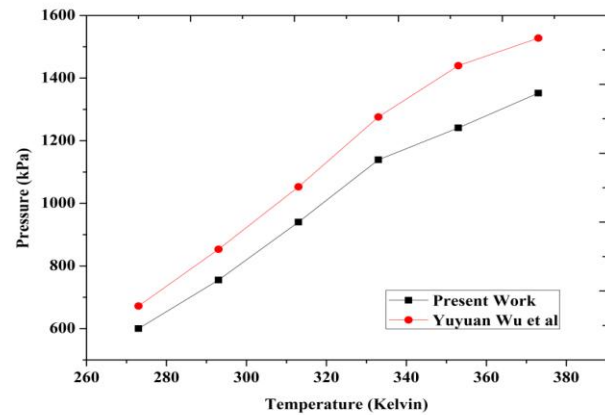


Fig.1: Validation of pressure obtained for Lithium Bromide-Water mixture at Ammonia mass fraction of 25% and Lithium Bromide mass fraction of 50%

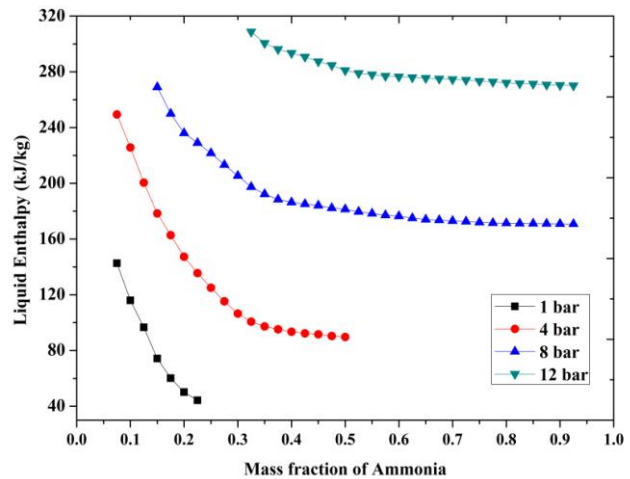


Fig.2: Variation of Liquid Enthalpy of Ammonia-Water mixture with that of Ammonia mass fraction at different pressure

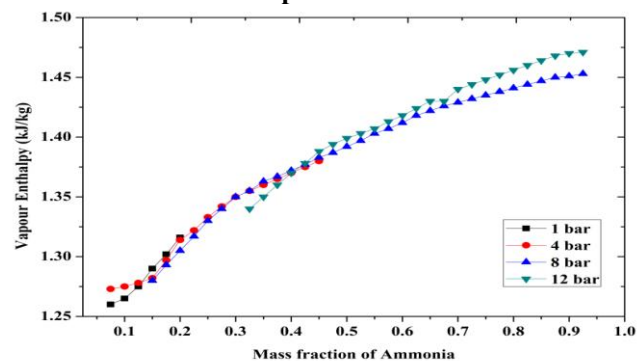


Fig.3: Variation of Vapour Enthalpy of Ammonia-Water mixture with that of Ammonia mass fraction at different pressure

The Fig. 4 shows that the liquid mixture entropy decreases with increase in liquid mass fraction of ammonia. The enthalpy is reduced by adding ammonia and the degree of randomness in the binary mixture also reduces after evolving heat due to exothermic reaction.

But increase in pressure, leads to increase in specific heat and enthalpy which in turn causes increase in liquid mixture entropy. Fig.5 shows the increase in mixture vapour entropy with increase in ammonia liquid mass fraction. It can also be seen that the entropy decreases in increase in pressure. The vapour formed is less at higher pressures. This results in increase in saturation point. High enthalpy is required to form the vapour resulting in increase in entropy. At higher pressures, the vapour formation is suppressed, resulting in large enthalpy to break the molecules in to vapour. The ammonia and water reaction is an exothermic process and leads to increase in saturation point leading to increase in surface tension. The force required to brake the bond is higher due to elevation in saturation point. The vapour diffusivity increases with increase of liquid ammonia mass. But the diffusivity decreases at higher pressures due to the low vapour formation. Vapour diffusivity into the mixture also decrease with increase in liquid ammonia. Therefore, the entropy decreases at higher pressures.

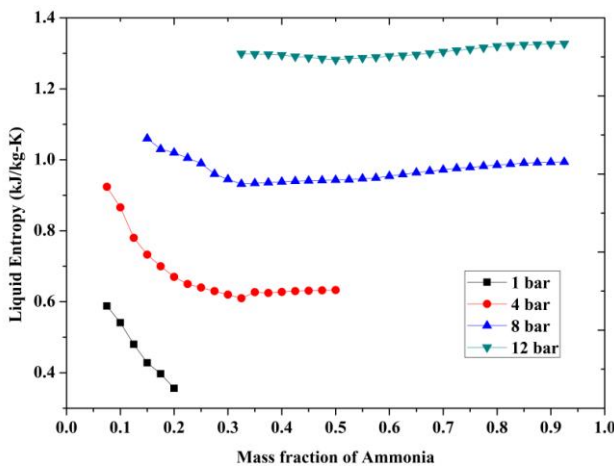


Fig.4: Variation of Liquid Entropy of Ammonia-Water mixture with that of Ammonia mass fraction at different pressure

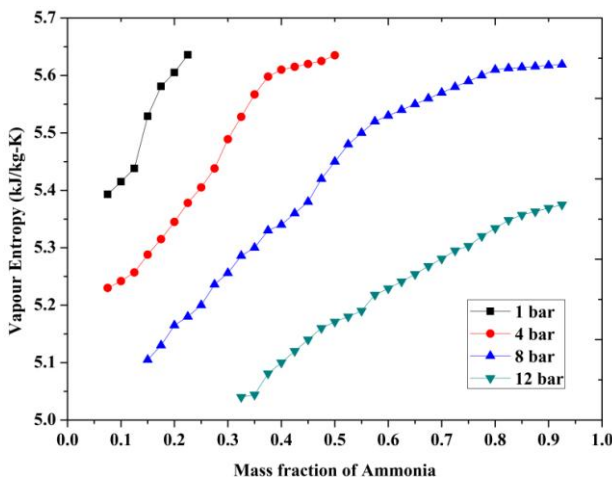


Fig.5: Variation of Vapour Entropy of Ammonia-Water mixture with that of Ammonia mass fraction at different pressure

Fig.6 shows increase in liquid mixture enthalpy with both increase in temperature and as well as increase in lithium bromide salt addition. Li^+ ion of the salt has capacity to absorb more water i.e OH^- ions. It is also exothermic reaction and elevates the saturation point. This results in high enthalpy to brake the molecules of Li^+ and water. Increase in temperature increases the enthalpy due to rise in specific heat. Fig.7 shows the increase in liquid mixture entropy with both increase in temperature and as well as increase in lithium bromide. Fig.8 shows the increase in liquid ternary mixture enthalpy with increase in ammonia-water mixture mass fractions and increase in ternary mixture liquid enthalpy with increase in temperature. Addition of ammonia and lithium bromide to water is a highly exothermic reaction, which is a negative deviation from Raoult's law, increasing the saturation point. The Li^+ ion can absorb more the water molecules and in turn water molecules attract more NH_4^+ molecules. This results in destruction of ammonia-water equilibrium relation also. The specific heat increases, leading to increase in enthalpy also

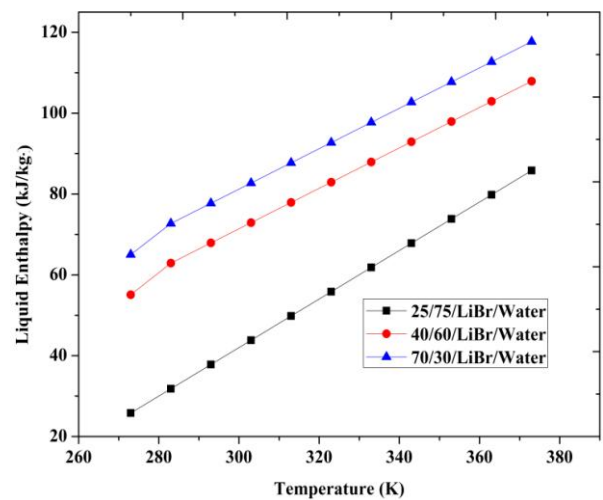


Fig. 6: Variation of Liquid Enthalpy of Lithium Bromide-Water mixture with that of Temperature at various concentration of Lithium bromide

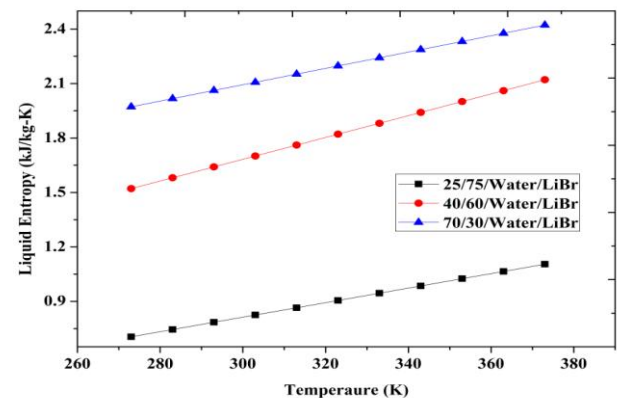


Fig.7: Variation of Liquid Entropy of Lithium Bromide-Water mixture with that of Temperature at various concentration of Lithium bromide

Fig. 9 shows that the liquid ternary mixture enthalpy increases with increase in temperature and decreases with increasing LiBr- mass fractions for constant mass fraction of ammonia of 22.5 %. Fig.10 shows the same trend as Fig.10, but mass fraction of ammonia is 10% in this case.

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The Li^+ attracts more the OH^- of water, which in turn OH^- attracts NH_4^+ ion of ammonia. This leads to exothermic reactions leading to decrease in the liquid mixture ternary enthalpy.

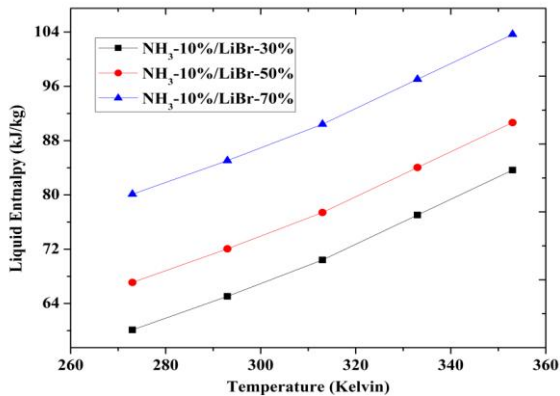


Fig.8: Variation of Enthalpy of Ammonia-Lithium Bromide-Water ternary mixture with that of Temperature at various concentration of Lithium bromide

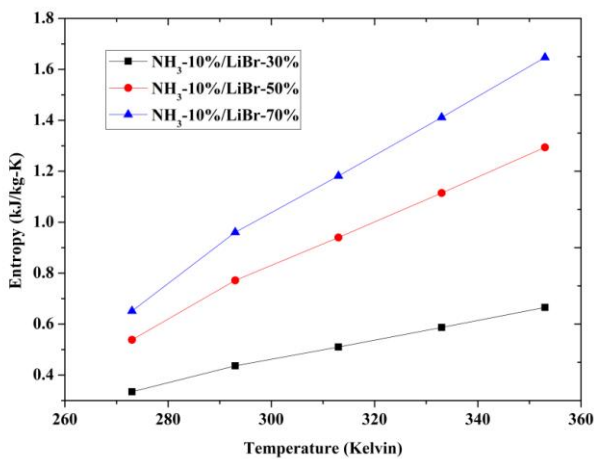


Fig. 9: Variation of Entropy of Ammonia-Lithium Bromide-Water ternary mixture with that of Temperature at various concentration of Lithium bromide

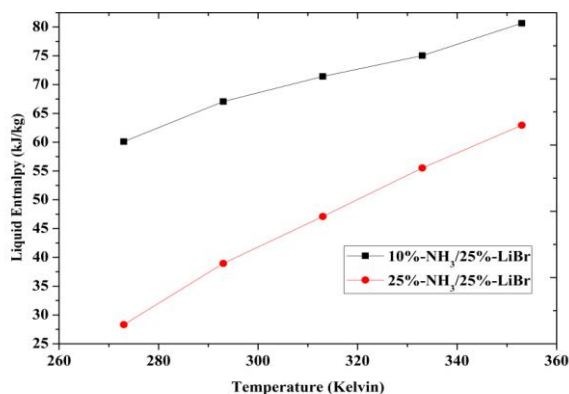


Fig.10: Variation of Enthalpy of Ammonia-Lithium Bromide-Water ternary mixture with that of Temperature at different concentration of Ammonia

Fig. 11 shows the increase in ternary liquid mixture enthalpy with increase in temperature and decrease with increase in addition of lithium bromide salt solution. The Li^+ ion has more tendency to attract OH^- ion of water molecules and is also highly exothermic than ammonia water reaction. The

equilibrium of ammonia and water is destroyed because of the Li^+ ions in LiBr. This leads to decrease in ternary liquid mixture enthalpy due to release of energy after reaction. Addition of ammonia and lithium bromide to water is a highly exothermic reaction, which is a negative deviation from Raoult's law, increasing the saturation point. The enthalpy decreases after releasing energy and decreases entropy. The Li^+ ion can absorb more the water molecules and the water molecules attract more NH_4^+ molecules. This results in destruction of ammonia-water equilibrium relation also. The specific heat increases and exothermic reaction takes place, leading to decrease in the liquid mixture ternary enthalpy. Entropy decreases due to decrease in enthalpy, as the total heat content reduces.

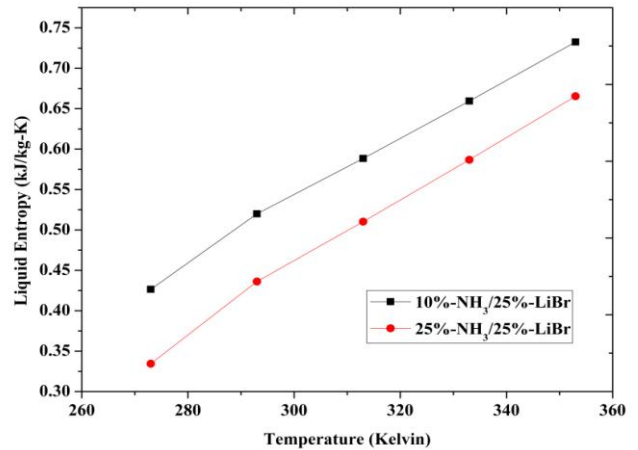


Fig.11: Variation of Entropy of Ammonia-Lithium Bromide-Water ternary mixture with that of Temperature at different concentration of Ammonia

IV. CONCLUSIONS

A set of computational formulations of thermodynamic and Thermophysical properties of Ammonia-Water, Water-Lithium bromide and Ammonia-Water-Lithium Bromide solutions at different pressures and temperatures are presented in the paper. Obtained results are validated with the experimental data which were available in the literature. Following conclusions are arrived from the present study:

- Liquid enthalpy and entropy increases with increase in ammonia concentration and the pressure for ternary mixture of Lithium bromide-water-Ammonia at constant lithium bromide concentration.
- Liquid enthalpy and entropy increases with increase in lithium bromide concentration and the pressure for ternary mixture of Lithium bromide-water-Ammonia at constant ammonia concentration.
- Increase in enthalpy and entropy is more significant in increase in lithium bromide concentration than that of increase in ammonia concentration because The Li^+ ion has more tendency to attract OH^- ion of water molecules and is also highly exothermic than ammonia-water reaction

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