



Original Research Article

Formulation of Correlations for Calculating Densities and Thermal Conductivities of an Ammonia-Water Solution

*¹Mumah, S.N., ¹Akande, H.F., ¹Mudi, K.Y., ²Olaniyan, I.O. and ¹Samuel, F.

¹Department of Chemical Engineering, Kaduna Polytechnic, Kaduna, Kaduna State, Nigeria.

²Department of Civil Engineering, Kaduna Polytechnic, Kaduna, Kaduna State, Nigeria.

*mumahsdoi@kadunapolytechnic.edu.ng

<http://doi.org/10.5281/zenodo.5805223>

ARTICLE INFORMATION

Article history:

Received 28 Jun, 2021

Revised 10 Nov, 2021

Accepted 16 Nov, 2021

Available online 30 Dec, 2021

Keywords:

Density

Thermal conductivity

Absorption refrigeration

Ammonia-water system

Correlation

ABSTRACT

Liquid and vapour density and thermal conductivity values are essential properties necessary for designing and simulating ammonia-water refrigeration systems. Previous works on the estimation of these thermodynamic properties have shown varying results. It is therefore necessary to develop correlations that can accurately depict the variations of these properties with relevant variables and compare the results with experimental data. This paper presented procedures for developing correlations for the pure components and then used the correlations to generate liquid and vapour densities and thermal conductivity values for the solution of the mixture. The values were compared with experimental data. Comparing the values generated from the correlations for liquid density with two sets of experimental data values gave average percentage deviations of $\pm 2.18\%$ and $\pm 3.12\%$. For vapour solution densities, the average percentage deviation was $\pm 1.23\%$. For liquid thermal conductivity, the average percentage deviations were $\pm 3.67\%$, $\pm 4.82\%$, and $\pm 0.076\%$ for data provided by Baranov, Shamsetdinov and Conde-Petit respectively. For vapour thermal conductivity, the data generated showed increasing deviations from 1.43% to a maximum of 12.8% when compared with the data generated by Conde-Petit for the pressure values considered. Without taking vapour conductivity into account, the low maximum percentage deviations for the calculated values for liquid density, liquid thermal conductivity and vapour thermal conductivity indicated that the correlations and procedures presented in this study could be used to calculate values of these properties.

© 2021 RJEES. All rights reserved.

1. INTRODUCTION

It has been established that the density (ρ) and thermal conductivity (λ) values for vapour and liquid ammonia-water solution vary considerably over the temperature and pressure ranges normally encountered

in ammonia-water absorption refrigeration system (Conde-Petit, 2006). Establishing accurate correlations for these properties over these ranges are crucial for proper design and simulation purposes.

Many of the correlations used for the calculation of these properties are generated based on theoretical basis. In many cases, the accuracy of these correlations has not been established. Therefore, it is not possible to show how this affects the design and simulation of an ammonia-water refrigeration system (Chakrabarti and Blessing, 2015). Determination of the properties of pure components usually is not complicated. However, for a solution of two or more components, pressure and temperature variations and the impact of the mixing effect come into play. For density and thermal conductivity of an ammonia-water solution, the variation of these properties are more pronounced for the vapour than for the liquid (Tillner-Roth and Friend, 1998). Determination of the accuracy of correlations is, therefore, a critical factor for proper design and simulation.

The Tait equation which has undergone many modifications, has been used over the years for liquid density calculation (Hayward, 1967). One such modification is by Thomson *et al.* (1982), who extended and generalized the Tait equation to calculate compressed fluid densities at very high pressures. The new correlation gave very low deviations from experimental values for nonpolar liquids, polar and quantum liquids. However, they can only be applied for pure components. Another theoretical equation for calculating liquid density is the Rackett equation (Rackett, 1970), which Spencer and Danner (1972) modified to make applicable to a large number of the mixtures. However, the modified equation was found to be less accurate for polar mixtures. A more precise model for calculating liquid density is the COSTALD (COrrsponding STate Liquid Density) density correlation. It has been determined that it is more accurate than the McCarty-Klosek-Mckinley and Rackett-Spencer-Danner correlations (Shanshool and Hashim, 2001; NIST ThermoData Engine, 2017). However, the COSTALD density equation is not simple and produces less accurate results for temperatures close to the critical point and polar mixture. Many other empirical and semi-empirical models exist to calculate vapour density, but most are for pure compounds (Kud *et al.*, 2020). Generally, assuming the mixture as quasi-ideal gives satisfactory results for the calculation of liquid and vapour densities. Most of the correlations for calculating density are not based on any particular physical model and so are considered theoretical. Examples of such models include Klosek-Mckinley (Klosek and Mckinley, 1968) and McCarty correlations (McCarty, 1980). These correlations take into effect the temperature variation but not the pressure. McCarty (1980) modified the Klosek-Mckinley correlation by considering the nitrogen content of the mixture. Though more accurate than the Klosek-Mckinley correlation, it was limited by its composition and temperature ranges.

Many correlations have been presented to calculate the thermal conductivities of the liquid mixture. As pointed out by Afshar (1981), many of the models used to predict the thermal conductivity of ammonia are accurate enough to be used to calculate the thermal conductivities of mixtures containing ammonia. Prominent among these are Filippov (1955), Jamieson *et al.* (1975), Baroncini *et al.* (1981, 1983, 1984), Lin and Pate (1992) and power law method correlations (Haj-Kacem *et al.*, 2017). The requirement for the listed method is the thermal conductivities of the pure constituents. Conde-Petit (2006) noted that ammonia-water liquid thermal conductivities show varying degrees of inconsistency. With that, it is difficult to formulate correlations to calculate liquid thermal conductivities. Conde-Petit (2006) proposed a quasi-ideal correlation to calculate thermal conductivity. This model will be applied in this paper as it is a well-tested one. Baranov (1997) provided graphical values of thermal conductivity of ammonia-water liquid mixtures for temperatures up to 460 K and selected concentration. However, experimental values were not made available and can only be approximated from the plots. Shamsetdinov *et al.* (2013) generated experimental data for thermal conductivity of ammonia-water solution from 278 K to 356 K and pressures up to 200 bar and developed models to fit the experimental data. An average percentage deviation of 6.6% was found when data generated by the model were compared with experimental values. Wassiljewa (1904) presented an equation to calculate the thermal conductivity values of vapour mixtures at low pressure. Mason and Saxena (1958) proposed a modified version of Wassiljewa (1904). Louro (2008) studied the modified equation's accuracy in calculating this property compared with experimental results and found out that the average percentage deviation was significantly low. However, accurate equations for pure components are required.

With varying accuracies of inconsistencies for density and thermal conductivity correlations from literature when compared to experimental values, it is necessary to develop more correlations from pure component data and determine the accuracy of fit with various experimental data. Therefore, the purpose of this paper is to develop empirical correlations supported by confirmatory data for the calculation of density and thermal conductivity of ammonia-water solution for the liquid and vapour phases. Correlations for calculating these properties for an ammonia-water solution shall be generated from experimental data of pure components. The accuracy of these correlations shall be determined by comparing the data output from these equations with experimental data and those generated from other studies.

2. METHODOLOGY

2.1. Data Sources

Many experimental data exist in the literature, but these sources should be verified before use. For water, experimental data are authenticated by the International Association for the Properties of Water and Steam (IAPWS). The liquid density values for pure water were generated using the method recommended by IAPWS R6-95 (2018). Density values of pure saturated ammonia vapour were extracted from Cragoe *et al.* (1923) and regressed. Experimental values for the thermal conductivity of water were extracted from Shamsetdinov *et al.* (2013) and Baranov (1997), while those for liquid ammonia were generated from Cragoe *et al.* (1923). The data for vapour thermal conductivity were extracted from Shamsetdinov *et al.* (2013).

2.2. Formulation of Correlations

The density values of pure ammonia liquid were extracted from Haar and Gallagher (1978). Calculated liquid density values of ammonia were validated with values obtained from Tillner-Roth and Friend (1998) correlations, while data generated from the procedure presented here were compared with data generated by Conde-Petit (2006). For ammonia-water vapour, Conde-Petit (2006) assumed a quasi-ideal mixture of real gas mixture for ammonia-water vapour solution and introduced an excess density correction to calculate the density of the mixture. This procedure was applied in this study using new correlations for pure components. Data generated were validated with those generated by Conde-Petit (2006). Kaern *et al.* (2015) recommended the method presented Conde-Petit (2006) for the liquid thermal conductivity. These methods compare the best with the experimental data from Baranov (1997) and Jamieson *et al.* (1975), which was applied in this study. Kaern *et al.* (2015) compared data of vapour thermal conductivities using a simple mole fraction average, a modification of the Mason and Saxena (1958) method, and procedures presented by Stecco and Desideri (1992), El-Sayed (1988), and Conde-Petit (2006). For the vapour thermal conductivity, Kaern *et al.* (2015) recommended the application of the Mason and Saxena (1958) method. This method was also recommended by Conde-Petit (2006) and El-Sayed (1988) and was applied in this study. All correlations for pure components were developed using Microsoft Excel Correlation development procedure while those of ammonia-water solutions are developed using the proportional node three-parameters plot procedure (Mumah, 1991).

2.2.1. Correlations for liquid density of an ammonia-water solution

Conde-Petit (2006) presented a quasi-ideal solution procedure to calculate the density of an ammonia-water liquid solution (ρ_{sol}). This is represented by Equation (1).

$$\rho_{sol} = x\rho_{NH_3 T_{NH_3}^*} + (1-x)\rho_{H_2O T_{H_2O}^*} + \Delta\rho_{T_m, x}^{\ddagger} \quad (1)$$

Where $\rho_{NH_3 T_{NH_3}^*}$ is the density of pure ammonia in kg/m^3 calculated at T^* of ammonia, $\rho_{H_2O T_{H_2O}^*}$ is the density of pure water calculated at T^* of water, and $\Delta\rho_{T_m, x}^{\ddagger}$ is the excess density value.

To correct for non-ideality, the excess density value ($\Delta\rho_{T_m, x}^{\ddagger}$) value was added. This was calculated from Equation (2).

$$\Delta\rho_{T_m^{\dagger},x} = x(1-x) - Ax^2(1-x)\rho_{NH_3 T_{NH_3}^*}^{0.5}\rho_{H_2O T_{H_2O}^*}^{0.5} \quad (2)$$

Where:

$$T_{m,x}^{\dagger} = \frac{T_m}{T_{c,H_2O}} \quad (3)$$

The parameter A was calculated from Equation 4 (Conde-Petit, 2006).

$$A = \sum_{i=0}^2 A_{1,i} T_m^{\dagger i} + 1/x \left(\sum_{i=0}^2 A_{2,i} T_m^{\dagger i} \right) \quad (4)$$

Where A_1 and A_2 are defined in Table 1 for various values of i in Equation (4):

Parameter	Index		
	$i=0$	$i=1$	$i=2$
A_1	-2.410	8.310	-6.924
A_2	2.118	-4.050	4.443

The T^* in Equation (2) for water and ammonia are calculated as follows (Conde-Petit, 2006).

$$T_{c,H_2O} = 647.15K; T_{c,NH_3} = 405.15K$$

Where T_c is the critical temperature for the various components. Conde-Petit (2006)'s equation represents the critical temperature of the mixture shown in Equation (5).

$$T_{c,m} = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 \quad (5)$$

Where: $a_0 = 647.14$, $a_1 = -199.822371$, $a_2 = 109.035522$, $a_3 = -239.626217$ and $a_4 = 88.689691$

$$\tau = 1.0 - T_m/T_{c,m} \quad (6)$$

where τ is the reduced temperature compliment to unity, T_m is the temperature of the mixture and $T_{c,m}$ is the critical temperature of the mixture.

$$T_{NH_3}^* = \theta T_{c,NH_3} \quad (7)$$

$$T_{H_2O}^* = \theta T_{c,H_2O} \quad (8)$$

Where T_{c,NH_3} is the critical temperature of pure ammonia, T_{c,H_2O} is the the critical temperature of pure water and θ is the reduced temperature. The reduced temperature is calculated from Equation (9).

$$\theta = T_m/T_{c,m} \quad (9)$$

New correlations were generated for the pure components, and the procedure presented was applied to calculate the liquid density of the ammonia-water solution.

2.2.2. Correlations for vapour densities of ammonia-water solution

Just like for liquid density, the vapour is considered quasi-ideal. Therefore, Conde-Petit (2006) presents the procedure used to calculate vapour density values for the mixture.

$$\rho_m = y\rho_{NH_3 T_{NH_3}^*} + (1-y)\rho_{H_2O T_{H_2O}^*} + \Delta\rho_{T_m^{\dagger},y} \quad (10)$$

Where $\rho_{NH_3 T_{NH_3}^*}$ is the vapour density of pure ammonia (kg/m^3) calculated at $T_{NH_3}^*$, $\rho_{H_2O T_{H_2O}^*}$ is the vapour density of pure water calculated at $T_{H_2O}^*$ and $\Delta\rho_{T_m^{\dagger},y}$ is the excess density.

Equation (11) gives the value of the excess density:

$$\Delta\rho_{T_m^\ddagger, y} = A(-y)^B (1 - e^{Cy^D}) \Delta\rho_{m, T_m^\ddagger} \quad (11)$$

where A, B, C, D, J and K are parameters.

$$\Delta\rho_{m, T_m^\ddagger} = e^{J-K/T_m^\ddagger} \quad (12)$$

Where:

$$T_m^\ddagger = \frac{T_m}{T_{c, H_2O}} \quad (13)$$

Where the parameters are given as $A=82.0, C=-0.05, J=9.952, B=0.5, D=2.75$ and $K=3.884$

$T_{H_2O}^*$ and $T_{NH_3}^*$ are calculated following the procedure shown from Equations (10) to (13).

As was done in the case of liquid density, new correlations were generated for the pure components and the procedure presented above was applied to calculate the density of ammonia-water vapour.

2.2.3. Correlations for liquid thermal conductivity

Conde-Petit (2006) proposed a quasi-ideal correlation to calculate thermal conductivity as shown in Equation (14).

$$\lambda_m = x\lambda_{NH_3}(\rho_{NH_3}^+) + (1-x)\lambda_{H_2O}(T_{H_2O}^*) \quad (14)$$

where λ_m is the thermal conductivity of the liquid mixture in $Wm^{-1}K^{-1}$, λ_{NH_3} is the thermal conductivity of pure ammonia liquid and λ_{H_2O} is the thermal conductivity of pure water. T^* was calculated from the procedure presented in Conde-Petit (2006) (Equations (7) and (8)), and the density parameter ($\rho_{NH_3}^+$) is calculated from Equation (15) (Conde-Petit, 2006).

$$\rho_{NH_3}^+ = \rho_{NH_3}(T_{NH_3}^*)x^{0.425} \quad (15)$$

With the thermal conductivity values of the pure components, that of the solution was calculated by applying Equations (14) and (15).

2.2.4. Correlations for vapour thermal conductivities

The modified Wassiljewa (1904) equation by Mason and Saxena (1958) was used in this paper to correlate the vapour thermal conductivity of an ammonia-water solution. This is presented as follows:

$$\lambda_m = \frac{y\lambda_{NH_3}}{y + (1-y)\varphi_{12}} + \frac{(1-y)\lambda_{H_2O}}{(1-y) + y\varphi_{2,1}} \quad (16)$$

where λ_m is the thermal conductivity of the vapour mixture in $Wm^{-1}K^{-1}$, λ_{NH_3} is the thermal conductivity of pure ammonia vapour and λ_{H_2O} is the thermal conductivity of pure steam.

φ_{12} and $\varphi_{2,1}$ were calculated from the following auxiliary equations.

$$\varphi_{12} = \frac{\left[1 + \left(\frac{\eta_{NH_3}}{\eta_{H_2O}}\right)^{0.5} \left(\frac{M_{H_2O}}{M_{NH_3}}\right)^{0.25}\right]^2}{\left[8 \left(1 + \frac{M_{NH_3}}{M_{H_2O}}\right)\right]^{0.5}} \quad (17)$$

$$\varphi_{2,1} = \varphi_{12} \frac{\eta_{H_2O} M_{NH_3}}{\eta_{NH_3} M_{H_2O}} \quad (18)$$

Where M is the molecular weight for the components ($M_{H_2O} = 18.02$, and $M_{NH_3} = 17.03$) and η_{NH_3} is the viscosity of pure ammonia vapour and η_{H_2O} is the viscosity of pure steam. η_i is the pure component viscosity in Pa.s and y_i is the mole fraction.

The temperatures are calculated for pure ammonia and pure water at known pressures using the simplified correlation of Patek and Klomfar (1995). The temperature to use in this process is obtained by iteration from Equation (19). Once the pressure is known, then the temperature can be determined from the correlation by Patel and Khomfar (1995) presented in Equation (19).

$$T(py) = T_0 \sum_i a_i (1-y)^{m/4} \left[\ln \left(\frac{p_0}{p} \right) \right]^{n_i} \quad (19)$$

Where T is the temperature in K calculated at a known pressure and vapour concentration, y is the ammonia mole fraction of the vapour and P is the pressure in MPa. The parameters i , m , n and a are given in Table 2.

Table 2: parameters for ammonia-water vapour correlation

i	Parameters		
	m_i	n_i	a_i
1	0	0	$+0.324\ 004 \times 10^1$
2	0	1	$-0.395\ 920 \times 10^2$
3	0	2	$+0.43\ 5624 \times 10^{-1}$
4	0	3	$-0.218\ 943 \times 10^{-2}$
5	1	0	$-0.143\ 526 \times 10^1$
6	1	1	$+0.105\ 256 \times 10^1$
7	1	2	$-0.719\ 281 \times 10^{-1}$
8	2	0	$+0.122\ 362 \times 10^2$
9	2	1	$-0.224\ 368 \times 10^1$
10	3	0	$-0.201\ 780 \times 10^2$
11	3	1	$+0.110\ 834 \times 10^1$
12	4	0	$+0.145\ 399 \times 10^2$
13	4	2	$+0.644\ 312 \times 10^0$
14	5	0	$-0.221\ 246 \times 10^1$
15	5	2	$-0.756\ 266 \times 10^{00}$
16	6	0	$-0.135\ 529 \times 10^1$
17	7	2	$+0.183\ 541 \times 10^0$
$T_0 = 100\ K$		$P_0 = 2\ MPa$	

As can be seen from Equations (17) and (18), there is a need for dynamic viscosity values for pure ammonia and water. Therefore, with thermal conductivity and dynamic viscosity values of the pure components, the value for ammonia-water vapour were calculated by applying Equations (16) to (19).

3. RESULTS AND DISCUSSION

3.1. Liquid Density

Conde-Petit (2006) used a different procedure to calculate the density of pure constituents. In this paper, a different set of equations which are considered more accurate are used. The density of pure water is calculated from Equation (20) using $T_{H_2O}^*$.

$$\rho_{H_2O} = a_1 T^6 + a_2 T^5 + a_3 T^4 + a_4 T^3 + a_5 T^2 + a_6 T + a_7 \quad (20)$$

Where $a_1 = -9.031 \times 10^{-12}$; $a_2 = 2.3572302 \times 10^{-08}$; $a_3 = -2.5271885494 \times 10^{-05}$; $a_4 = 0.014237361079319$; $a_5 = -4.446432939499160$; $a_6 = 729.744030889966$; $a_7 = -48149.866657815$

To calculate density of pure ammonia liquid, the correlation presented by Cragoe *et al.* (1923) was used.

$$V = \text{Absolute Value of } (133.0 - (T - 273.15)) \quad (21)$$

$$D = \frac{4.2830 + 0.813055V^{0.5} - 0.0082861V}{(1.0 + 0.424805V^{0.5} + 0.015938V)} \quad (22)$$

and

$$\rho_{NH_3} = \left(\frac{1.0}{D}\right) 1.0 \times 10^{+03} \quad (23)$$

With the values of the density of the pure components from Equations (20) to (23), that of ammonia-water liquid solution was then calculated by applying Equations (1) to (9). Figure 1 shows the plot of the liquid density generated from the correlations for varying mass fractions and temperatures. As shown in Figure 1, the density of ammonia-water liquid solution decreases with increasing ammonia mass fraction in the solution. However, it decreases with increasing temperature for the temperature range considered (273.15 K to 413.15 K). This decrease is expected as heating causes the molecules to spread apart, thereby occupying a larger volume. This trend is corroborated by data provided by Tillner-Roth and Friend (2000) and Conde-Petit (2006).

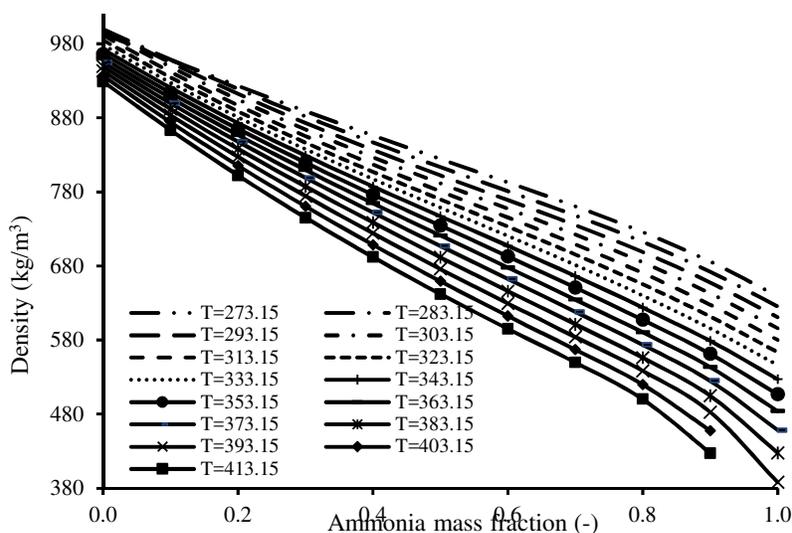


Figure 1: Variation of liquid density of ammonia-water solution with ammonia mass fractions and temperatures

3.2. Vapour Density

The vapour densities for ammonia vapour and steam are calculated from Equations (24) and (25).

$$\rho_{NH_3} = -8.085 \times 10^{-09}T^3 + 1.4017842 \times 10^{-05}T^2 - 0.008674579053T + 2.2533906 \quad (24)$$

$$\rho_{H_2O} = 5.7352 \times 10^{-14}T^6 - 1.22443969 \times 10^{-10}T^5 + 1.14232983291 \times 10^{-07}T^4 - 5.7741952571 \times 10^{-05}T^3 + 0.016417059T^2 - 2.472906T + 153.8366 \quad (25)$$

With the values generated from Equations (24) and (25), Equations (10) and (13) were applied to generate the density of the ammonia-water vapour. Figure 2 shows the plot of the vapour density generated from the

correlations for varying mass fractions and temperatures. For vapour properties, the plot is for various pressures since it affects the properties significantly. For liquids, the effect of pressure is insignificant. Reviewing Figure 2, it can be seen that for a particular pressure, the vapour density increases as the ammonia concentration in the vapour increases for the concentration range of 0.0wt 5 to 0.75 wt %) and then starts to decrease. The increase in vapour density with pressure is expected as the molecules are more densely packed as the pressure increases. This trend is followed for each pressure. As reflected in Figure 2, pressure is a major factor in determining the vapour density value. The vapour density values and variation trends compare satisfactorily with data provided by Conde-Petit (2006).

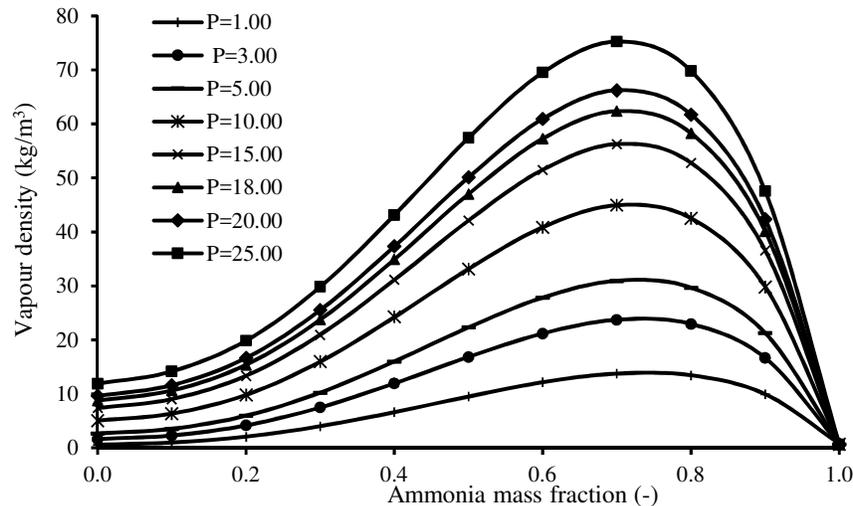


Figure 2: Variation of vapour density of ammonia-water solution with ammonia mass fractions and temperatures

3.3. Liquid Thermal Conductivity

The thermal conductivity of the pure components are represented by Equations (26) and (27).

$$\lambda_{NH_3} = 2551.30 - 376.62 \times 10^{-02}T - 29.35x 10^{-04}T^2 \quad (26)$$

$$\lambda_{H_2O} = -916.62 + 1254.73 \times 10^{-02}T - 152.12x 10^{-04}T^2 \quad (27)$$

For ammonia-water solutions, the contributions of the thermal conductivity of each component are considered. Therefore, the liquid thermal conductivity can be expressed for pure ammonia and water as follows:

$$f_{NH_3} = 2551.30 - 376.62 \times 10^{-02}T - 29.35x 10^{-04}T^2 \quad (28)$$

$$f_{H_2O} = -916.62 + 1254.73 \times 10^{-02}T - 152.12x 10^{-04}T^2 \quad (29)$$

Where f_{NH_3} and f_{H_2O} are now considered as contributing factor parameters for ammonia and water, respectively.

$$\text{if } f_{NH_3} > f_{H_2O} : A = \lambda_{NH_3}$$

$$\text{if } f_{NH_3} > f_{H_2O} : B = \lambda_{H_2O}$$

$$\text{if } f_{NH_3} > f_{H_2O} : X = x_m$$

where x_m is the mass fraction of ammonia in the ammonia-water solution.

$$\text{if } f_{NH_3} \leq f_{H_2O} : A = \lambda_{H_2O}$$

$$\text{if } f_{NH_3} \leq f_{H_2O} : B = \lambda_{NH_3}$$

$$\text{if } f_{NH_3} > f_{H_2O} : X = 1 - x_m$$

The liquid thermal conductivity of an ammonia-water solution is then given by Equation (30).

$$\lambda_m = (X^{1.5}(A-B) + B)4.187 \times 10^{-07} \quad (30)$$

Figure 3 shows the plot of the liquid thermal conductivity generated from the correlations for varying mass fractions and temperatures. From Figure 3, it can be seen that the thermal conductivity decreases with increasing ammonia mass fraction in the solution. However, for the temperature range considered (273.15 K to 413.15 K), concentration is a factor in determining trends as the temperature increases. As depicted in Figure 3, it can be seen that for the ammonia mass fraction of 0.4 and above, the thermal conductivity of the ammonia-water liquid solution decreases with increasing temperature. However, for the concentration range of 0.0 to 0.4 wt%, no particular trend in the thermal conductivity values can be determined as the temperature increases. Also, it can be seen from Figure 3 that variation of thermal conductivity values across the full ammonia concentration range (0.0-1.0 weight %) increases as the temperature increases. Liquid thermal conductivity decreases with increasing temperature because the molecules move further apart, causing lattice distortion, making it difficult for electrons to flow. These trends and variations are corroborated by data presented by Jamieson *et al.* (1975) and Baranov *et al.* (1996).

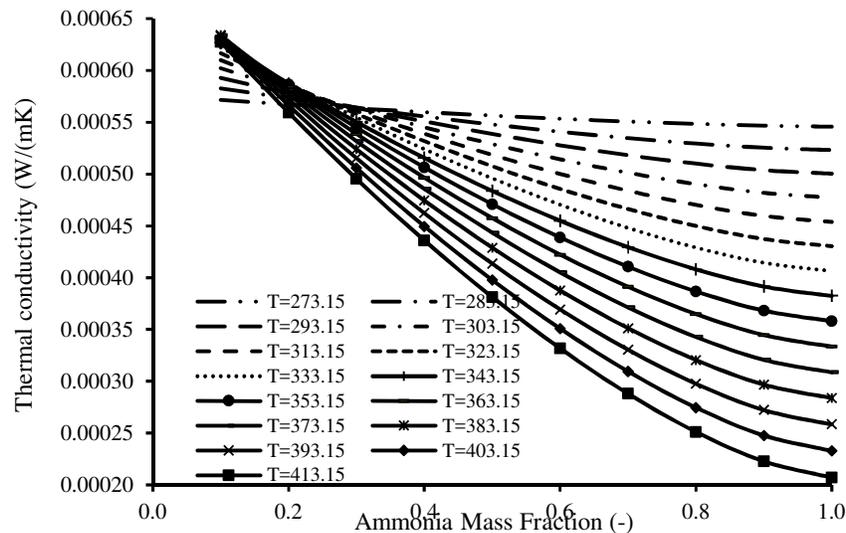


Figure 3: Variation of liquid thermal conductivity of ammonia-water solution with ammonia mass fractions and temperatures

3.4. Vapour Thermal Conductivity

To calculate the thermal conductivity of ammonia-water vapour, the viscosity value is required. For ammonia, dynamic viscosity varies with pressure. The dynamic viscosity of ammonia liquid is calculated as follows:

For 1 bar:

$$\eta_{NH_3} = A = 1.0 \times 10^{-06} (0.0000006945T^2 + 0.0372754397T - 0.9978816765) \quad (31)$$

For 10 bar:

$$\eta_{NH_3} = B = 1.0 \times 10^{-06} (-0.000005161T^2 + 0.043983183T - 2.823490380) \quad (32)$$

For 50 bar:

$$\eta_{NH_3} = C = 1.0 \times 10^{-06} (-0.000007561T^2 + 0.047034914T - 3.559091860) \quad (33)$$

For 100 bar:

$$\eta_{NH_3} = C = 1.0 \times 10^{-06} (0.0000631751T^2 - 0.040451258T + 23.530440411) \quad (34)$$

The thermal conductivity at any pressure in the range can be calculated by simple interpolation.

For $1.0 < P < 10$ bar:

$$\eta_{NH_3} = \left(\frac{P - 1.0}{10.0 - 1.0} \right) * (B - A) + A \quad (35)$$

For $10.0 < P < 50.0$ bar:

$$\eta_{NH_3} = \left(\frac{P - 10.0}{50.0 - 10.0} \right) * (C - B) + B \quad (36)$$

For $50.0 < P < 100$ bar:

$$\eta_{NH_3} = \left(\frac{P - 50.0}{100.0 - 50.0} \right) * (D - C) + C \quad (37)$$

For water, the dynamic viscosity is not affected significantly by pressure changes. Therefore, the dynamic viscosity was calculated using Equation (38).

$$\eta_{H_2O} = 1.0 \times 10^{-06} (a_1 T^4 + a_2 T^3 + a_3 T^2 + a_4 T + a_5) \quad (38)$$

Where the parameters are given as follows:

$$a_1 = 5.206 \times 10^{-9}; a_2 = -8.689180 \times 10^{-6}; a_3 = 0.005343692335; a_4 = -1.393363694257; a_5 = 138.479875602456;$$

The thermal conductivity of ammonia-water vapour is generated by applying Equations (31) to (38). Figure 4 shows the plot of the thermal conductivity of ammonia-water vapour generated from the correlations for varying mass fractions and temperatures. As is the case for vapour density, the plot is for various pressures since pressure affects the properties significantly. For liquids, the effect of pressure is insignificant. As can be seen in Figure 4, the vapour thermal conductivity increases with increasing pressure for a particular ammonia concentration in the ammonia-water vapour. However, it decreases with increasing ammonia concentration in the vapour for a specific pressure. As was the case with vapour density, pressure plays a significant factor in determining the value of the thermal conductivity of ammonia-water vapour. As the pressure increases, the molecules in the vapour become more densely packed, increasing thermal conductivity. The vapour thermal conductivity values and variation trends compare satisfactorily with data provided by Conde-Petit (2006).

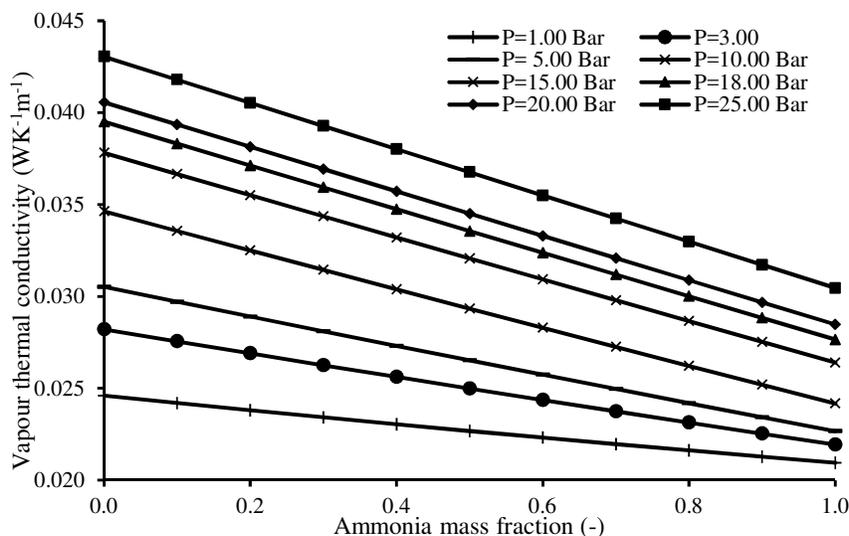


Figure 4: Variation of vapour thermal conductivity of ammonia-water solution with ammonia mass fractions and pressures

Table 3 summarises coefficient of determination (R^2) which compares the experimental values and values from regression analysis generated from the correlations. The regressions analysis for pure components gives a very high level of accuracy ($R^2 > 0.99$), which is typically expected. Comparing the data for liquid density with those generated by Conde-Petit (2006) and Tillner-Roth and Friend (2000) gives an average percentage deviation of $\pm 2.18\%$ and $\pm 3.12\%$, respectively. This is considered low, and so the correlations can be applied for the calculation of liquid density. This also shows that the Cragoe *et al.* (1923) equation for calculating the density of liquid ammonia is still satisfactorily accurate.

Comparing the data generated for vapour solution densities with those generated by Conde-Petit (2006) provides an average percentage deviation of $\pm 1.23\%$. Conde-Petit (2006) did not provide the accuracy of the method used. Presently only quasi-ideal methods exist to calculate vapour density, and since this value is low, its use is also recommended. Comparing the data generated for vapour solution densities with those generated by Conde-Petit (2006) gives an average percentage deviation of $\pm 1.23\%$.

For liquid thermal conductivity, the average percentage deviation when generated values are compared with data generated by Baranov (1997), Shamsetdinov *et al.* (2013), and Conde-Petit (2006) were $\pm 3.67\%$, $\pm 1.82\%$ and $\pm 0.076\%$, respectively. Data was extracted from the plot provided in Baranov (1997) and not from actual experimental values since they are unavailable. The low percentage deviation between the procedure presented in this study and those of the three data sources indicate that the correlations can be applied to calculate the thermal conductivity of liquid ammonia-water solutions.

Correlating vapour thermal conductivity of ammonia-water solution with the model used in this paper requires accurate correlation depicting the mixture property and good correlations for dynamic viscosity and thermal conductivity of the two components, ammonia and ammonia water. These stages contribute to the percentage deviations when data generated by the correlations are compared with experimental values. The vapour thermal conductivity data generated were compared to those of Conde-Petit (2006). For vapour thermal conductivity, the data generated showed increasing deviations from 1.23% to a maximum of 12.8% when compared with the data generated by Conde-Petit (2006) for all the pressures values considered. Experimental data for the temperature regime (204K – 247K) used for the calculation of ammonia thermal conductivity could not be found to conduct an effective comparison of the final model. The evaluated data from the correlations were further compared with the experimental data presented by Shamsetdinov *et al.*

(2013) and produced a maximum percentage deviation of 1.2%. This value is, however, only at 1.0 bar and so is limited.

Table 3: Comparison of correlated values with experimental data

Properties	Data sources	R ² and maximum % deviation values
Liquid density (kg/m ³)	IAPWS R6-95 (2018)-(Water)	0.999
	Haar and Gallagher (1978) – Ammonia	0.996
	Conde-Petit (2006)	±2.18% (Max. % deviation)
	Tillner-Roth and Friend (2000)	±3.12% (Max. % deviation)
Vapour density (kg/m ³)	IAPWS R6-95 (2018) – Water vapour	0.999
	Cragoe <i>et al.</i> (1923) – Ammonia	0.998
	Conde-Petit (2006)	±1.23% (Max. % deviation)
Liquid thermal conductivity (W/m-K)	IAPWS R15-11 (2011) -Water	0.999
	Cragoe (1923) – Ammonia	0.998
	Baranov (1997)-(ammonia-water solution)	±3.67% (Max. % deviation)
	Shamsetdinov <i>et al.</i> (2013) – ammonia	±1.82% (Max. % deviation)
	Conde-Petit (2006) – Ammonia-water solution	±0.076%(Max. % deviation)
Vapour thermal conductivity (W/m-K)	IAPWS R15-11(2011) – Water vapour	0.996
	Shamsetdinov <i>et al.</i> (2013) – Ammonia	0.999
	Conde-Petit (2006) (ammonia-water solution)	12.8% (Max. % deviation)
	Shamsetdinov <i>et al.</i> (2013) - (ammonia-water solution at 1 bar)	1.2% (Max. % Deviation)

4. CONCLUSION

This paper has developed correlations for the pure components and then used the correlations to generate liquid and vapour mixture density and thermal conductivity values. Detailed steps have been proposed for the calculation of each thermodynamic property. The values of the properties generated from these correlations have been compared with experimental data from the literature. Comparing the data for liquid density with those generated by Conde-Petit (2006) and Tillner-Roth and Friend (2000) produces an average percentage deviation of ±2.18 % and ±3.12 %, respectively. Comparing the data generated for vapour solution densities with those generated by Conde-Petit (2006) gives an average percentage deviation of ±1.23 %. For liquid thermal conductivity, the average percentage deviation when generated values are compared with experimental data generated by Baranov (1997), Shamsetdinov *et al.* (2013), and Conde-Petit (2006) are ±3.67 %, ±1.82 %, and ±0.076 %, respectively. The vapour thermal conductivity data generated were compared to those of Conde-Petit (2006). There was a progressive deviation increase to a maximum of 12.8 % as the ammonia mass fraction increases for all pressures considered. Apart from vapour thermal conductivities, the values of the properties generated by the procedures presented in this paper show low percentage deviations when compared with experimental values from the literature. Therefore, it is

recommended that they be used to calculate these properties relevant to the design and thermodynamic analysis of an ammonia-water refrigeration system.

5. ACKNOWLEDGEMENT

The authors wish to acknowledge the funding provided for this research work by Tertiary Education Trust Fund (TETFund) under the National Research Fund (NRF) Grants. REF: TETF/R&D/CE/NRF/POLY/KADUNA/VOL. 1/B5).

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

- Afshar, R.S., Murad, S. and Saxena, S.C. (1981). Thermal conductivity of gaseous ammonia in the temperature range 358-925 K. *Chemical Engineering Communications*, 10, pp. 1-3.
- Baranov, A.N. (1997). The investigation of ammonia -water gas and liquid mixture properties. In: Friend, D.G., Haynes, W.M. (Eds.), Report on the Workshop on Thermophysical Properties of Ammonia/Water Mixtures, NISTIR-5059. Boulder, Colorado.
- Baroncini, C., Di Filippo, P., Latini, G. and Pacetti, M. (1981) Organic liquid thermal conductivity: A prediction method in the reduced temperature range 0.3 to 0.8. *International Journal of Thermophysics*, 2, pp. 21-38
- Baroncini, C., Di Filippo, P. and Latini, G. (1983). Comparison between Predicted and Experimental Thermal Conductivity Values for the Liquid Substances and the Liquid Mixtures at Different Temperatures and Pressures, Paper presented at the Workshop on Thermal Conductivity Measurement, IMEKO, Budapest, pp. 14–16.
- Baroncini, C., Latini, G. and Pierpaoli, P., (1984). Thermal conductivity of organic liquid binary mixtures: Measurements and prediction method. *International Journal of Thermophysics*, 5, pp. 387–401.
- Conde-Petit, M. (2006). Thermophysical Properties of NH₃/H₂O Mixtures for the Industrial Design of Absorption Refrigeration Equipment. A formulation for Industrial Use. M. Conde Engineering, Zurich, Switzerland
- Chakrabarti, A. and Blessing, L. (2015). A review of theories and models of design. *Journal of the Indian Institute of Science*, 95(4), pp. 325-340
- Cragoe, C.S., McKelvey, E.C. and O'Connor, G.F. (1923). Specific Volume of Saturated Ammonia Vapor. *Scientific Paper- Bureau of Standards*. 18, 655
- El-Sayed, Y. M. (1988). On Exergy and Surface Requirements of Heat Transfer Processes Involving Binary Mixtures. *ASME WAM*, Nov. 27 - Dec. 2 1988, Chicago, IL, AES Vol. 6, HTD Vol. 97, pp. 19-24.
- Filippov, L. (1955). *Chemical Abstract*, 50: 8276, 1956. As cited in: The Properties of Gases and Liquids, R.C. Reid, J.M. Prausnitz, B.E. Poling, McGraw-Hill, Inc, 5th Ed. 1987.
- Haar, L. and Gallagher, J.S. (1978). Thermodynamic properties of ammonia. *Journal of Physical and Chemical Reference Data*, 7, pp. 635-792
- Haj-Kacem, R.B. Herráez, J.V., Al-Arfaj, A.A., Alkhalidi, M.A., Alzamil, N.O., and Ouerfelli, N. (2017). Correlation analysis of the power law parameters for viscosity of some engineering fluids; *Physics and Chemistry of Liquids*, 55(6), pp. 766-774
- Hayward, A. T. J. (1967). Compressibility equations for liquids: a comparative study. *British Journal of Applied Physics*, 18 (7), pp. 965
- IAPWS R6-95 (2018). *Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use*. September 2018
- IAPWS R15-11 (2011). Release on the IAPWS Formulation 2011 for the Thermal Conductivity of Ordinary Water Substance. September 2011
- Jamieson, D. T., Irving, J. B. and Tudhope, J. S. (1975). *Liquid Thermal Conductivity. A Data Survey to 1973*, H. M. Stationary Office, Edinburgh.

- Kaern, M. R., Modi, A., Jensen and J. K., and Haglind, F. (2015). An assessment of transport property estimation methods for ammonia–water mixtures and their influence on heat exchanger size. *International Journal of Thermophysics*, 36(7), pp. 1468-1497.
- Klosek, J. and McKinley, C. (1968). Densities of liquefied natural gas of low molecular weight hydrocarbons, *Proceedings of the First International Conference and Exhibition of Liquefied Natural Gas*, , Institute for Gas Technology, Chicago.
- Kud, A., Christophe C. and Stefan, M. (2020). A new semi-empirical model for saturated vapor density of pure compounds. *Journal of Chemical and Engineering Data*, 65(2), pp. 577-590.
- Lin, J. Y. and Pate, M. B. (1992). A Thermal conductivity prediction method for refrigerant mixtures in the liquid phase. *Proceedings of the 1992 International Refrigeration Conference: energy efficiency and new refrigerants : July 14-17, 1992, Purdue University, West Lafayette, Indiana, USA*. .
- Louro, C. S. C. (2008). Thermal Conductivity of Gases: Transient Hot-Wire Method. Masters Thesis, Instituti Superior Tecnico, Universidade Tecnico de Lisboa.
- Mason, E. A. and Saxena, S. C. (1958). Approximate formula for the thermal conductivity of gas mixtures, *The Physics of Fluids*, 1(5), pp. 361-369.
- McCarty, R. D. (1980). Four mathematical models for the prediction of LNG densities", *NBS Technical Note 1030*, National Bureau of Standards, Boulder, CO
- Mumah, S.N. (1991). *Simulation and Optimization of Solar-powered and Hybrid Heat Pump System for cooling*. Zaria: PhD Thesis, Department of Chemical Engineering, Ahmadu Bello University
- NIST ThermoData Engine (2017). Equations for pure components density [online]. Available electronically at https://trc.nist.gov/TDE/TDE_Help/Eqns-Pure-DensityLG/COSTALD.htm. Accessed on 20th of January, 2021
- Patek, J. and Klomfar, J. (1995). Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system. *International Journal of Refrigeration*, 18(4), pp. 228-234.
- Rackett, B. G. (1970). Equation of state for saturated liquids. *Journal of Chemical Engineering Data*. 15(4), pp. 514-517.
- Shamsetdinov, F.N., Zaripov, Z.I., Abdulagatov, I.M., Huber, M.L., Gumerov, F.M., Gabitov, F.R. and Kazakov, A.F. (2013) Experimental study of the thermal conductivity of ammonia -water refrigerant mixtures at temperatures from 278 K to 356 K and at pressures up to 20 MPa. *International Journal of Refrigeration*, 36, pp. 1347-1368
- Shanshool, A.F. and Hashim, E. T. (2001). A generalized equation of state to predict oil-stock density. *Petroleum Science and Technology*, 19, pp. 3-4.
- Spencer, C. and Danner, R. (1972). Improved Equation for Prediction of Saturated Liquid Density, *Journal of Chemical Engineering Data*, 17(2), pp. 236-241.
- Stecco, S.S. and Desideri, U. (1992). Considerations on the design principles for a binary mixture heat recovery boiler. *Journal of Engineering Gas Turbines Power*, 114, pp. 701–706.
- Thomson, G.H, K. Brobst, R., and Hankinson, R. W. (1982). An improved correlation for densities of compressed liquids and liquid mixtures. *AIChE Journal*, 28(4), pp. 671-676.
- Tillner-Roth, R., and Friend, D. G. A. (1998). Helmholtz free energy formulation of the thermodynamic properties of the mixture {water + ammonia}. *Journal of Physical and Chemical Reference Data*, 27(1), pp. 63–96.
- Wassiljew, A. (1904). Wärmeleitung in Gasgemischen. *Physikalische Zeitschrift*, 5, p. 737.