Density Measurement of Aqueous solution of Tetrapropylammonium Hydroxide at different Temperatures and Concentrations: Data and Correlation

Nur Ani kartikawati; Bhajan Lal; Muhammad Ibrahim Bin Abdul Mutalib; Suriati Bt Sufian; Azmi Mohd Shariff.
Chemical Engineering Department Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar Perak, Malaysia.

Email: bhajan.lal@utp.edu.my

Abstract. Densities of aqueous Tetrapropylammonium hydroxide solution (5, 10, 15, 20 and 25 wt %) were investigated over a temperature range of 298.15 to 333.15 K and at atmospheric pressure. Derived properties, molar volume ($V_m$) and excess molar volumes ($\tilde{V}_m$) were estimated and correlated with temperature using the least square method. The predicted values from correlations are in good agreement with measured values. The obtained results from derived properties for a binary system, $\tilde{V}_m$ are interpreted based on intermolecular interactions.

Keywords: Density, Thermal expansion, Excess molar volume, and TPAOH

1. Introduction

The emission of greenhouse gases, particularly CO2 has been considered as a major concern for environment. It causes increasing of global temperature which arise climate change fear. CO2 separation by absorption using aqueous amines solutions is the most extensively used method due to its wide operating experience in the industry and technical maturity. Even have many limitation of problems faced in CO2 absorption such as corrosion, foaming, solvent degradation and volatility[1]. Ionic Liquids have attracted considerable interest recently, due to their unique physical and chemical properties include low vapour pressure, high thermal stability, and good solvent for wide range of organic and inorganic compounds [2].

Thermo physical properties of absorbent are necessary to characterize the solvents used in industrial applications. These properties are also essential in the design of treatment equipment of the acid gas removal. [3], [4]. The density parameter is crucial for physical solubility of CO2. Anabella, et al., (2012) Have measured density with speed of sound for aqueous imidazolium-based ionic liquids at different temperatures [5]. Their density result found to decrease with an increase in temperatures. Govinda et al., (2015), has done about the effect of the alkyl chain length of the cation on the interactions between water and ammonium-based ionic liquids at 25 °C [6]. These obtained results declared that the ammonium-based ILs significantly affect the intermolecular interactions between the solvent molecules. Further Kartikawati et al., (2018) have measured density along with other physicochemical properties for aqueous solution of Ammonium based ionic liquids over a wide range of temperatures (295.15 to 333.15 K) [7]. The studied property is found to decrease with an increase in temperatures. Zhang et al., (2013) investigated the densities were increased linearly with a decrease in temperature and be higher than the density of water [8]. Machanova et al., (2012) reported the effect of
temperature and the alkyl chain length on involved properties. They found that the density and viscosity decrease with temperature as opposed to conductivity [9]. Given that the density is crucial in absorption process, due the aqueous solution of Tetrapropylammonium hydroxide is potential solvents for CO$_2$ capture, as well as the density data for aqueous TPAOH (Tetrapropylammonium Hydroxide) solution and comparison with conventional solvent at different temperatures is limited, it is very interesting to investigating about density of aqueous solution of TPAOH.

In the present study, the density of TPAOH solutions over temperature range (298.15 to 333.15 K) and concentration 5, 10, 15, 20 and 25 wt %) have been studied and reported. Density data is also used to calculate other properties such as excess molar volume, and coefficient of thermal expansion. From the data obtained can be used to propose an accurate estimate of the temperature and concentration solvent for CO$_2$ capture.

2. Experimental Section

2.1. Material
TPAOH (purity ≥99.00%) was acquired from Sigma-Aldrich. Deionized water is used to prepare different (5, 10, 15, 20 and 25 wt %) concentrations of TPAOH solution. Samples were prepared and weighed using an analytical balance with the accuracy of ±0.1 mg. All the solvent were kept in airtight bottles.

2.2. Density Procedure measurement
The densities of the TPAOH aqueous solutions are measured at temperatures ranged from 298.15 to 333.15 K using Anton Paar DMA-5000 digital vibrating tube density meter with an accuracy of ±0.0006 g·cm$^{-3}$. The measuring cell temperature is adjusted using a built-in solid state thermostat, which maintains a temperature having an exactness of ±0.01 K. The densities reported using an average of three measurements. Before used, the equipment was calibrated with a standard water of Millipore quality.

3. Result and discussion
The density of TPAOH aqueous solution prepared with different concentrations (5, 10, 15, 20 and 25 wt %) at a temperature range between of 298.15 to 333.15 K was measured.

![Figure 1](image-url). Graph of experimental data of density of aqueous TPAOH solution as a function of temperature for different concentration
The value of densities measurement of aqueous TPAOH solution is shown in Fig. 1. An inverse relationship is observed as the density is seen to increase with the decrease of temperature. The same trend has been reported in the literature [10]–[12]. By increasing the temperature, the molecules tend to migrate further apart as the kinetic energy within each molecule increases with an increase in the temperature [13]. It later was found that the experimental data regarding the density of aqueous TPAOH solutions are in the range of 0.965–0.995 g·cm\(^{-3}\) at various concentrations (5, 10, 15, 20 and 25 wt %)

![Figure 2](image)

**Figure 2.** Comparison the density of literature data [maham 1993) for aqueous solution of MEA (a) with the experiment data of aqueous solution of TPAOH (b). and●, 298.15 K, ■, 303.15 K; ♦, 313.15 K;▲, 323.15 K;□, 333.15 K.

From the Fig.2, it can be seen that MEA and TPAOH aqueous solutions have different behavior for different concentration. For MEA the density increase with the increase of concentration while TPAOH showed different behavior. The results can be demonstrated based on the high interaction molecule between MEA and water. MEA has strong attractive forces to water molecules which reduce the intermolecular space, and the total volume of the solution can be smaller than the combined volume of its components, leading to an extra increase in density [14], [15]. For TPAOH solutions, the increasing of concentration means a higher amount of bulk molecules with hydrophobic alkyl chain are incorporated into the system. Thus, density is decreased [1].

**Table 1.** Correlation equation parameters and SD for densities \(\rho/(g\cdot cm^{-3})\) of TPAOH aqueous solution.

| Cons (wt%) | \(\rho_{(exp)}\) | T(K)       | A0     | A1      | R2   | \(\rho_{(predic)}\) | SD       |
|-----------|-----------------|------------|--------|---------|------|-------------------|----------|
| 0.99663   | 298.15          | 1.1383     | -0.0005| 1       | 0.989225 | 0.0077753    |
| 0.99418   | 303.15          |            |        |         | 0.986725 |
| 0.989448  | 313.15          |            |        |         | 0.981725 |
| 0.984774  | 323.15          |            |        |         | 0.976725 |
| 0.979937  | 333.15          |            |        |         | 0.971725 |
| 5         | 0.99596         | 298.15     | 1.1412 | 0.00055 | 0.9998  | 0.992125     | 0.0035824|
|           | 303.15          |            |        |         | 0.989625 |

3
The density correlated with temperature using Eq (1). The values of densities and the corresponding coefficients are presented in Table 2.

\[ \rho = A_0 + A_1 (T) \]  

(1)

Where \( \rho \) is density, \( A_0 \) and \( A_1 \) are correlation parameters, and \( T \) is the temperature in Kelvin. The standard deviation (SD) of predicted density by equation one is calculated using Eq 2.

\[ SD = \left[ \frac{\sum (X_{exp} - X_{cal})^2}{n} \right]^{0.5} \]  

(2)

Where SD is standard deviation, \( X_{exp} \) is the value of experiment, \( X_{cal} \) is the estimated value, and \( n \) is some measure points. It can be observed from Table 2, \( R^2 \) value is higher than 0.95 which refer to the good agreement between experimental and predicted density. The density data and correlation parameter are used to calculate the coefficient of thermal expansion \( \alpha_p \) according to Eq. 3. This property quantifies the expansion of the material by temperature. Thermal expansion is also necessary for designing acid gas separation system [18].

\[ \alpha_p = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} = \frac{A_1}{A_0 + A_1 T} \]  

(3)

Where \( \alpha_p \) stand for the thermal expansion coefficient, \( T \) is temperature, \( \rho \) is density and \( A_0 \) and \( A_1 \) are correlation parameter in Eq 1. From the result shown in Table 3, \( \alpha_p \) increased with increasing temperature and concentration. It can be noted from Table 3 that the change in thermal expansion coefficients values affected slightly by temperature. Therefore, the variation of volume expansion of the studied solutions could be considered as independent of temperature. Meanwhile, adding more TPAOH sound to have higher thermal expansion due to weak bonding with water molecules compared with the water-water system.
Table 2. Coefficient of thermal expansion of aqueous solution of TBAOH

| T(K)  | 5 wt %     | 10 wt %    | 15 wt %    | 20 wt %    | 25 wt %    |
|-------|------------|------------|------------|------------|------------|
| 298.15| 0.1495143  | 0.1495131  | 0.1493096  | 0.1794072  | 0.1794046  |
| 303.15| 0.1520143  | 0.1520131  | 0.1520096  | 0.1824072  | 0.1824046  |
| 313.15| 0.1570143  | 0.1570131  | 0.1570096  | 0.1884072  | 0.1884046  |
| 323.15| 0.1620143  | 0.1620131  | 0.1620096  | 0.1944072  | 0.1944046  |
| 333.15| 0.1670143  | 0.1670131  | 0.1670096  | 0.2004072  | 0.2004046  |

The same trend has been investigated in the literature [15,19]. This property also is an advantage of TPAOH to be used as an absorbent for CO\textsubscript{2} capture system at a higher temperature so the thermal expansion in the absorbent can be avoided. The excess molar volume ($V_{m}^{E}$) of the solution is defined as the amount of volume which is in excess to that an ideal solution at the same conditions of the composition. For a binary system, $V_{m}^{E}$ can be calculated according to the following equation (Eq. 4) using mole fractions, molar masses, and densities to represent the volumes of solution and simple components [18].

$$V_{m}^{E} = \left[ x_2 M_2 \left( \frac{1}{\rho} + \frac{1}{\rho_2} \right) + \left( 1 - x_2 \right) M_1 \left( \frac{1}{\rho} - \frac{1}{\rho_2} \right) \right]$$

Where $V_{m}^{E}$ is excess molar volume; $\rho$ is the density of the aqueous solution, $\rho_2$ is the density of deionized water, $M_1$ is a molar mass of water, $M_2$ is a molar mass of solvent and $x_2$ is mole fraction of solvents. The excess molar volume results are tabulated in Table 4.

Tabel 3. Excess molar volume of aqueous solution of TPAOH

| T(K)  | 5 wt %      | 10 wt %     | 15 wt %     | 20 wt %     | 25 wt %     |
|-------|-------------|-------------|-------------|-------------|-------------|
| 298.15| 9.958458    | 9.950181    | 9.941879    | 15.978      | 15.91262    |
| 303.15| 9.921438    | 9.912889    | 9.903224    | 15.84434    | 15.75944    |
| 313.15| 9.846037    | 9.836455    | 9.819995    | 15.60283    | 15.49145    |
| 323.15| 9.766976    | 9.756355    | 9.737225    | 15.44546    | 15.30607    |
| 333.15| 9.681880    | 9.950181    | 9.644832    | 15.32206    | 15.18817    |

The results show a positive excess molar volume values in the presence of TPAOH. That can be attributed to physical properties, which are nonspecific interactions between the real species present in the mixture. The increase of excess molar volume is due to increasing dipole–dipole interactions which results strong in higher hydrogen bonding of components [19], [20].

Conclusion

In this paper, the densities of aqueous Tetrapropylammonium hydroxide solution (5,10, 15, 20 and 25 wt %) were investigated over a temperature range of 298.15 to 333.15 K and at atmospheric pressure. The experimental data for density measurement revealed that as the temperature of the solution increased the value of the density value decreased. Moreover, the density of the solution also decreased with the increase of TPAOH concentration. The behavior is opposite of MEA solution. Predicted values of density are shown good agreement with the experimental value. Increasing the
temperatures and concentrations is increasing the thermal expansion. The negative value of excess molar volume for the TPAOH aqueous solution decreased with increasing the temperature. Each physical property is correlated with temperature by the least square method, and the corresponding coefficients for each property are reported and used to predict the density.

Acknowledgment
The authors gratefully acknowledge Universiti Teknologi PETRONAS for providing the technical support to complete the present work.

References

[1] O. Nashed, J. C. H. Koh, and B. Lal, “Physical-chemical Properties of Aqueous TBAOH Solution for Gas Hydrates Promotion,” Procedia Eng., vol. 148, pp. 1351–1356, 2016.

[2] S. Garg, A. M. Shariff, M. S. Shaikh, B. Lal, A. Aftab, and N. Faiqa, “Selected physical properties of aqueous potassium salt of L-phenylalanine as a solvent for CO2capture,” Chem. Eng. Res. Des., vol. 113, pp. 169–181, 2016.

[3] S. N. Khan, S. M. Hailegiorgis, Z. Man, A. M. Shariff, and S. Garg, “Thermophysical properties of aqueous N-methyldiethanolamine (MDEA) and ionic liquids 1-butyl-3-methylimidazolium trifluoromethanesulfonate [bmim][OTf], 1-butyl-3-methylimidazolium acetate [bmim][Ac] hybrid solvents for CO2capture,” Chem. Eng. Res. Des., vol. 121, pp. 69–80, 2017.

[4] R. Umapathi, P. Attrit, and P. Venkatesu, “Thermophysical Properties of Aqueous Solution of Ammonium-Based Ionic Liquids,” J. Phys. Chem. B, vol. 118, no. 22, pp. 5971–5982, 2014.

[5] A. J. L. Costa et al., “Density , Thermal Expansion and Viscosity of Cholinium-Derived Ionic Liquids,” pp. 1–9, 2012.

[6] V. Govinda, P. Venkatesu, and I. Bahadur, Molecular interactions between ammonium-based ionic liquids and molecular solvents: current progress and challenges, vol. 18, no. 12. Royal Society of Chemistry, 2016.

[7] N. A. Kartikawati, R. Safdar, B. Lal, M. I. B. A. Mutalib, and A. M. Shariff, “Measurement and correlation of the physical properties of aqueous solutions of ammonium based ionic liquids,” J. Mol. Liq., vol. 253, no. 2017, pp. 250–258, 2018.

[8] M. Hou et al., “Thermodynamic properties of aqueous solutions of two ammonium-based protic liquids at 298.15 K,” J. Mol. Liq., vol. 178, pp. 149–155, 2013.

[9] J. Jacquemin, “Thermophysical Properties of Ammonium-Based Bis{(tri fluoromethyl)sulfonyl}imide Volumetric and Transport Properties,” 2012.

[10] K. A. Kurnia, F. Harris, C. D. Wilfred, M. I. Abdul Mutalib, and T. Murugesan, “Thermodynamic properties of CO2 absorption in hydroxyl ammonium ionic liquids at pressures of (100-1600) kPa,” Journal of Chemical Thermodynamics, vol. 41, no. 10. pp. 1069–1073, 2009.

[11] M. G. Montalbán, C. L. Bolivar, F. G. Diaz Baños, and G. Villora, “Effect of Temperature, Anion, and Alkyl Chain Length on the Density and Refractive Index of 1-Alkyl-3-methylimidazolium-Based Ionic Liquids,” J. Chem. Eng. Data, vol. 60, no. 7, pp. 1986–1996, 2015.

[12] R. L. Gardas, D. H. Dagade, J. a P. Coutinho, and K. J. Patil, “Thermodynamic studies of ionic interactions in aqueous solutions of imidazolium-based ionic liquids [Emim][Br] and [Bmim][Cl],” J. Phys. Chem. B, vol. 112, no. 11, pp. 3380–3389, 2008.

[13] P. Kilaru, G. A. Baker, and P. Scovazzo, “Density and surface tension measurements of imidazolium-, quaternary phosphoryl-, and ammonium-based room-temperature ionic liquids: Data and correlations,” J. Chem. Eng. Data, vol. 52, no. 6, pp. 2306–2314, 2007.
[14] T. G. Amundsen, L. E. Øi, and D. A. Eimer, “Density and Viscosity of Monoethanolamine + Water + Carbon Dioxide from (25 to 80) °C,” pp. 3096–3100, 2009.

[15] A. B. Pereiro, J. L. Legido, and A. Rodriguez, “Physical properties of ionic liquids based on 1-alkyl-3-methylimidazolium cation and hexafluorophosphate as anion and temperature dependence,” J. Chem. Thermodyn., vol. 39, no. 8, pp. 1168–1175, 2007.

[16] R. Safdar, A. A. Omar, L. B. Ismail, A. Bari, and B. Lal, “Measurement and correlation of physical properties of aqueous solutions of tetrabutylammonium hydroxide, piperazine and their aqueous blends,” Chinese J. Chem. Eng., vol. 23, no. 11, pp. 1811–1818, 2015.

[17] A. Muhammad, M. I. A. Mutalib, C. D. Wilfred, T. Murugesan, and A. Shafeeq, “Viscosity, refractive index, surface tension, and thermal decomposition of aqueous N-methyldiethanolamine solutions from (298.15 to 338.15) K,” J. Chem. Eng. Data, vol. 53, no. 9, pp. 2226–2229, 2008.

[18] S. Md Nayeem, M. Kondaiah, K. Sreekanth, and D. Krishna Rao, “Thermoacoustic, volumetric, and viscometric investigations in binary liquid system of cyclohexanone with benzyl benzoate at t = 308.15, 313.15, and 318.15 k,” J. Thermodyn., vol. 2014, 2014.

[19] N. Deenadayalu, S. Kumar, and P. Bhujrajh, “Liquid densities and excess molar volumes for (ionic liquids + methanol + water) ternary system at atmospheric pressure and at various temperatures,” J. Chem. Thermodyn., vol. 39, no. 9, pp. 1318–1324, 2007.

[20] G. H. Y. T. L. Chen, “Density, Viscosity and Excess Molar Volume of the Aqueous Ionic Liquid Tris (monoethanolamine),” pp. 2117–2132, 2014.