Thermal Conductivity of Aqueous Solvents Used in CO$_2$ Capture

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Abstract: The growing CO$_2$ concentration in the atmosphere forces researchers to work on improving existing carbon dioxide capture technologies. This technology is energy-intensive and consumes significant amount of heat for solvent regeneration. Thermal conductivity is a key property for the estimation of the heat required for solvents regeneration. Accordingly, in the present work thermal conductivity is measured for six aqueous solvent used for this purpose; monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2methyl-1-propanol (AMP), sodium hydroxide (NaOH), potassium carbonate (K$_2$CO$_3$), and potassium glycinate (PG) aqueous solutions for mole fraction range from 0.00 to 0.0825. The measurements were carried out at constant temperature (294.82K) and pressure (102.02kPa). The total experimental standard uncertainty of thermal conductivity, pressure, temperature, and mole fraction measurements were estimated to be ± 0.001 Wm^{-1}K^{-1}, ± 0.02kPa, ± 0.1K, and ± 0.0002, respectively. The measured values of thermal conductivity were compared with data and correlations reported in the literature. The average absolute deviation between measured and calculated values from available correlation equations for the thermal conductivity was lease than 0.5%.

Keywords: Thermal conductivity, amine solution, CO$_2$ capture, concentration.

1. INTRODUCTION

Removal of CO$_2$ from gas streams is one of the main gas separation processes in many industrial areas such as natural gas processing, flue gas treatment, biogas purification [1]. Physical and chemical absorption with absorbent liquids flowing through process unit such as absorption column, spray tower, gas - liquid membrane contactor are the most popular CO2 separation technique employed in the majority of currently undergoing researches and commercial projects [2]. In order to understand the feasibility for precise design of these absorption processes, comprehensive analysis of momentum, mass and heat transfer has to be carried out. For this purpose, accurate experimental data and theoretical models of transport properties such as thermal conductivity, viscosity and diffusion coefficient of these absorption liquids is important. An aqueous solutions of sodium hydroxide, potassium carbonate, amines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) is often employed as an absorbent liquids for CO$_2$ separation [3]. Moreover, some researchers were interested in potassium glycinate as an alternative solvent for CO$_2$ absorption because it has better stripping performance compared to conventional amines [4]. Several papers were published on thermo-physical properties of these absorbent liquids [5-13]. Thermal conductivity is an important parameter in the design of heat exchanger equipment and in the CO$_2$ gas absorption process to ensure that the process temperature is maintained. Comparing with other properties, only very little documents are available on the thermal conductivity of these liquids.

The aim of this work is to determine thermal conductivities of potential CO$_2$ absorption liquids including effects of concentration change of studied solvents. The results of the measurements were compared with the available literature data and empirical equations correlating solution composition and temperature. The results provide precise and reliable data regarding thermal conductivity six different solvent as a function of solvent mole fractions as a starting point for further investigation of the potential use of blended liquids in future work.

2. EXPERIMENTAL WORK

All chemicals involved in the present were acquired from commercial sources at analytical grade and used without further purification; detailed information is provided in Table **1**.

Distilled water was used for preparation of various aqueous solvent concentrations. All the experiments are performed at lab temperature and ambient pressure (~25°C and 1.0bar). Thermal conductivity measurements were performed with C-Therm TCI^{TM} thermal conductivity analyzer, Mathis, USA. The apparatus measures thermal conductivity of materials directly, based on the transient plane source method. The sensor is designed for the testing of liquids,

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Table 1: **Provenance and Mass Fraction Purity of Chemicals Used in this Study**

Chemical Name	Source Supply	State	Mass Fraction Purity[*]
Ethanol	Sigma Aldrich, Germany	Liquid	≥ 0.99
Toluene	Sigma Aldrich, Germany	Liquid	≥ 0.99
Monoethanolamine (MEA)	Sigma Aldrich, Germany	Liquid	≥ 0.99
Diethanolamie (DEA)	Sigma Aldrich, Germany	Liquid	≥ 0.99
2-amino-2methyl-1-propanol	Sigma Aldrich, Germany	Liquid	≥ 0.99
Sodium hydroxide (NaOH)	Sigma Aldrich, Germany	Pellets	≥ 0.99
Potassium carbonate (K_2CO_3),	Sigma Aldrich, Germany	Powder	≥ 0.99
Potassium glycinate (PG)	Sigma Aldrich, Germany	Powder	≥ 0.99

*as stated by supplier.

Table 2: **Comparison of Measure Thermal Conductivity with Literature Data**

T/K	Component	$\lambda / (\text{W.m}^{-1}.\text{K}^{-1})$			
		This work	Literature	Dev/%	Reference
298.5	Toluene	0.1310	0.1306	0.3	[14]
298	Ethanol	0.1661	0.1670	-0.5	[23]
295	Water	0.6015	0.6009	0.1	[15]

powders and solid materials. The liquid samples were tested by filling 50mL beaker to 35ml mark. The sensor is then placed in the beaker, no contact agent is required. The thermal conductivity analyzer requires no calibration or sample preparation. The system has broad testing capabilities (0.0 to 220W m^{-1} K^{-1}) in a wide range of temperatures (–50° to 200°C). In order to validate the data, the thermal conductivity of toluene, ethanol and water are measured and compared to literature values as shown in Table **2**.

3. RESULTS AND DISCUSSION

The thermal conductivity measured results for of six different absorbent solvents used in CO_2 absorption from natural gas. The values represent the thermal conductivity at air-conditioned lab temperature (294.83K) and pressure (102.01kPa). Figure **1** shows effect of mole fractions of aqueous solvents on the measured thermal conductivity. The results shown in Figure **1** illustrate that thermal conductivity of all aqueous solutions decreased with increased liquid concentrations, except for NaOH solution where the thermal conductivity increases with increasing concentration, this is attributed to the thermal conductivity of pure NaOH (0.688 /(W.m^{-1}.K^{-1}) is higher

than that of water (0.601/(W.m^{-1}.K^{-1}). Because values of thermal conductivity for most common organic liquids range between 0.1 and 0.2/(W.m^{-1}.K^{-1}) at temperatures below the normal boiling point, but water, ammonia, and other highly polar molecules have values several times as large [16]. At dilute concentrations near 0.01mol.l^{-1} the value of thermal conductivity approaches the thermal conductivity of water. The most common additive rule does not give the correct thermal conductivity value for liquid mixtures [17]. Many empirical correlation methods for
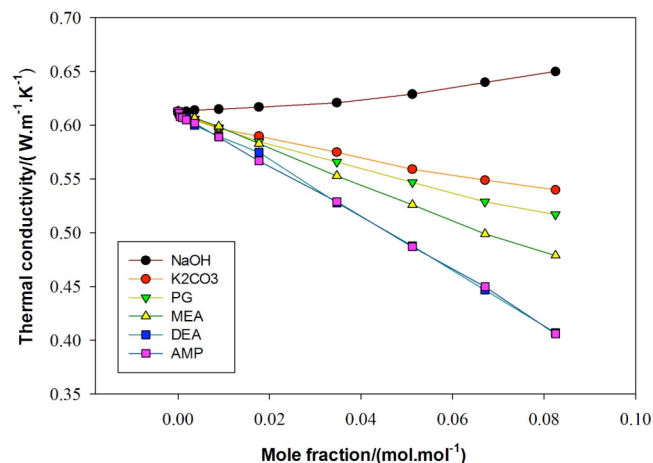

Figure 1: Thermal conductivity versus mole fraction of six different aqueous solvents.

thermal conductivity have been proposed. Many were for binary liquid mixtures. Some of popular correlations were selected here for discussion and the each absorbent liquid measured data were compared with those correlations.

3.1. Thermal Conductivity Correlations

The Filippov equation is [17]:

$$\lambda_{\mathrm{m}} = w_1 \lambda_1 + w_2 \lambda_2 - 0.72 w_1 w_2 (\lambda_2 - \lambda_1) \tag{1}$$

where w_1 and w_2 are the weight fractions of components 1 and 2. λ_1 and λ_2 are the pure component thermal conductivities. The components were so chosen that $\lambda_2 > \lambda_1$. The constant 0.72 may be replaced by an adjustable parameter if binary mixture data are available. The technique is not suitable for multicomponent mixtures but has been extensively tested for binary mixtures.

Losenicky equation is [18]:

$$\lambda = \sum_{i=1}^{n} \sum_{j=1}^{n} P_{ij} w_i \lambda_i \tag{2}$$

where $P_{ij} = k \bar{D}_i \bar{D}_j n_j$

where k is a proportionality factor, $\bar{D}$ is average cross sections of particular atoms or molecules, n is numbers of molecules of particular components of a solution and P_{ij} intensity of interaction of a molecule with another. Research and data evaluation at the National Engineering Laboratory has suggested for binary mixtures [19].

$$\lambda_m = w_1 \lambda_1 + w_2 \lambda_2 - \alpha (\lambda_2 - \lambda_1)[1 - (w_2)^{1/2}] w_2 \tag{3}$$

where w_1 and w_2 are weight fractions and, as in the Filippov method, the components are so selected that $\lambda_2 > \lambda_1$. α is an adjustable parameter that is set equal to unity if mixture data are unavailable for regression purposes. The authors indicate this correlation enables one to estimate mixture thermal conductivity within about 7% for all types of binary mixtures with or without water. It cannot, however, be extended to multicomponent mixtures. The following concentration dependence correlation for relative thermal conductivity of aqueous salt solutions was proposed by Chiquillo [20].

$$(\lambda_{\mathrm{sol}} / \lambda_{\mathrm{H_2O}}) = 1 + A_1 c + A_2 c^2 \tag{4}$$

where c is the molality, A_1 and A_2 are component specific constants. This equation was successfully used by several researchers. The calculated value of

the thermal conductivity from this equation shows no systematic deviations for concentrations up to 15% (wt). Above 15% (wt), the present data are higher than the calculated values. To calculate the thermal conductivity of dilute and moderately concentrated aqueous solutions, Riedel proposed the following equation [21].

$$\lambda_{\mathrm{sol}} = \lambda_{\mathrm{H_2O}} + \sum_i a_i c_i \tag{5}$$

where a_i and c_i are the coefficient for each ion and the concentration (molarity) of the electrolyte i. This equation is a statement of the additivity of individual ionic contributions in dilute solutions. Although the Riedel equation is applicable to multicomponent systems and can be used for dilute and moderately concentrated electrolyte solutions with good accuracy, it fails to represent experimental data over extended concentration ranges such as those commonly encountered for concentrated acids or alkaline solutions of NaOH or KOH [21].

3.2. Comparison between Correlations and the Experimental Data

Thermal conductivity of pure MEA is 0.3/(W.m⁻¹.K⁻¹) at 25°C [14]. The experimental and calculated thermal conductivity values for the aqueous solution of MEA for different concentration range from 0.01 to 5mol/l (0.02 to 8.25mol%). Figure **2** shows how the measured experimental data varies with different values calculated *via* correlation equations. Error bars are used to indicate the estimated error in a measurement. In other words, an error bar indicates the uncertainty in
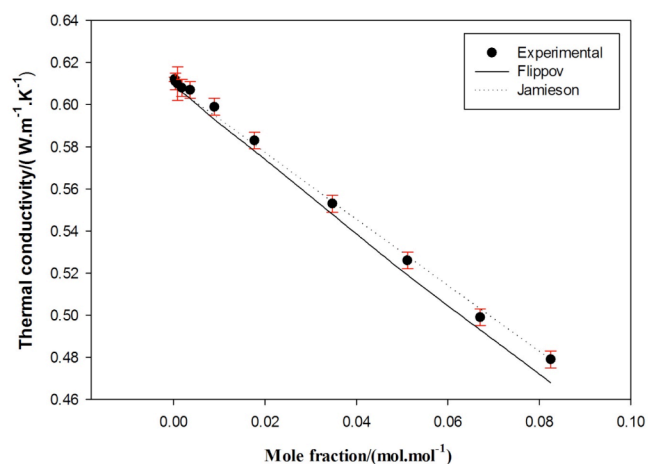

Figure 2: Comparison of experimental and calculated thermal conductivity versus mole fractions aqueous MEA solution.

a value. The Y-axis represents the column average, and the error bars represent the upper and lower errors. In the Filippov correlation if the constant value is 0.72 the deviation between experimental data and calculated values is very small. In the Jamieson correlation if adjustable parameter α is set equal to unity, the calculated thermal conductivity values well fit the experimental values.

Thermal conductivity of pure DEA is 0.180/$(W.m^{-1}.K^{-1})$ at 25°C [14]. The thermal conductivity of the experimental and the calculated values for the aqueous DEA solution for different concentration range from 0.01 to 5mol/l (0.02 to 8.25mol%). Figure **3** shows how the measured experimental data varies with different correlation calculated values. In the Filippov correlation if the constant value is 0.01 the deviation between experimental data and calculated values are
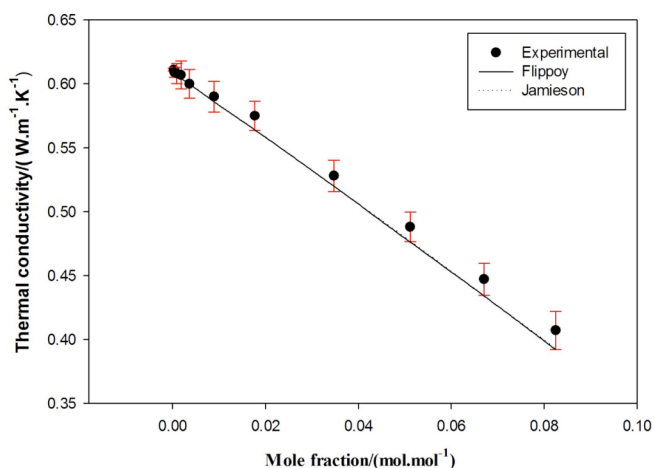

Figure 3: Comparison of experimental and calculated thermal conductivity versus mole fraction aqueous DEA solution.
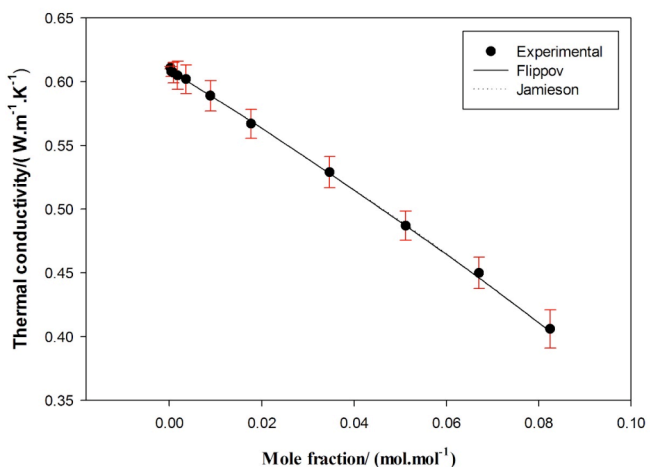

Figure 4: Comparison of experimental and calculated thermal conductivity versus mole fractions aqueous AMP solution.

very small. In the Jamieson correlation also if adjustable parameter α is set equal to 0.01, the calculated thermal conductivity values well fit the experimental values. Thermal conductivity of pure AMP is 0.165/$(W.m^{-1}.K^{-1})$ at 25°C [14]. The thermal conductivity experimental and calculated values for the aqueous solution of AMP for different concentration range from 0.0 to 5/$(mol.l^{-1})$ (0.0 to 8.25mole%). Figure **4** shows how the measured experimental data deviate from values calculated *via* available correlations. In the Filippov correlation if the constant value is 0.01 the deviation between experimental data and calculated values is very small. In the Jamieson correlation also if adjustable parameter α is set equal to 0.01, the calculated thermal conductivity values well fit the experimental values.

The thermal conductivity experimental and calculated values for the aqueous solution of NaOH for different concentration range from 0.01 to 5/$(mol.l^{-1})$ (0.02 to 8.25mol%). Figure **5** shows how the measured experimental data varies with different correlation calculated values. Chiquillo correlation shows the best agreement with experimental data for the selected concentration range. The value of constants were taken from literature [21]. To use Riedel correlation the ion constant values for Na^+ and OH^- are not available in the open literature. Also the experimental values were validated with NaOH Module software (Separators / LV Heat Atlas, 10th edition, Lauterbach Verfahrenstechni, Germany) to calculate physical properties of NaOH solution. The NaOH module determines the physical properties of aqueous sodium hydroxide (caustic soda) solutions in a temperature range of 20°C to 100°C with concentrations from 0 to 50 wt-% NaOH. The deviation
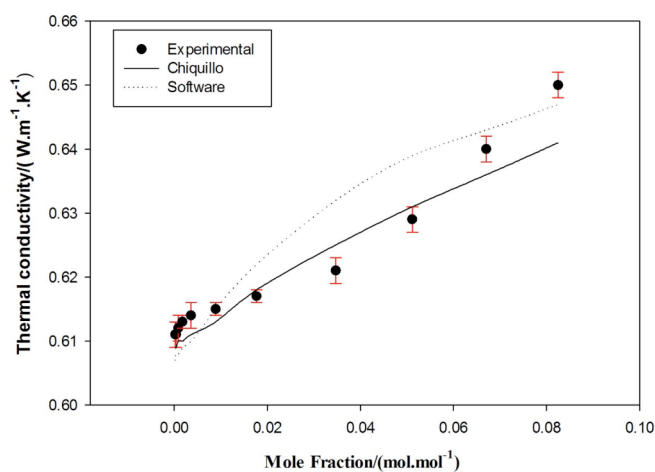

Figure 5: Comparison of experimental and calculated thermal conductivity versus mole fractions aqueous NaOH solution.

between experimental and calculated value is very small. The thermal conductivity experimental and calculated values for the aqueous solution of K_2CO_3 for different concentration range from 0.0 to 5/(mol.l^{-1}) (0 to 8.25mole%). The measured thermal conductivity of aqueous K_2CO_3 was compared with the literature data and was found to be in good agreement [22]. Figure **6** shows how the measured experimental data varies with different correlation calculated values. Chiquillo correlation best fits with experimental data only for low concentrations. The deviation between experimental and calculated value increases with concentration for concentrations above 1/(mol.l^{-1}). In contrast the Riedel correlation best fits with experimental data. Even at higher concentration the deviation is only 5. 28%.
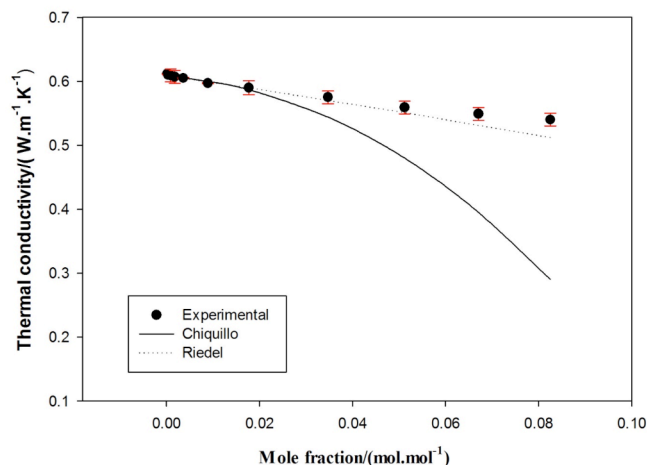

Figure 6: Comparison of experimental and calculated thermal conductivity versus mole fractions aqueous K_2CO_3 solution.
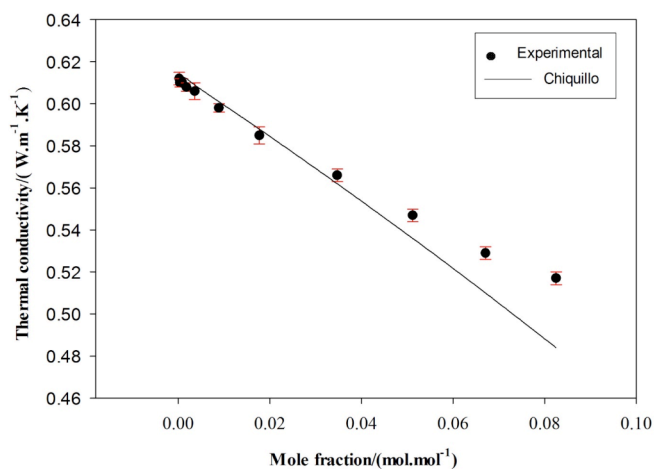

Figure 7: Comparison of experimental and calculated thermal conductivity versus mole fractions aqueous PG solution.

The thermal conductivity experimental and calculated values for the aqueous solution of PG for concentration range from 0 to 5/(mol.l^{-1}) (0 to 8.25mole%). Figure **7** shows how the measured experimental data varies with calculated values. As potassium glycinate (PG) is relatively new absorption liquid the studies on thermo physical properties of this liquid mixture is very rare. So an attempt was made to fit Chiquillo correlation and the constants were found as A_1 = -0.02607 and A_2 = 0.00144. With these constants Chiquiilo correlation calculated values best fit with experimental data.

CONCLUSIONS

The thermal conductivities of MEA, DEA, AMP, NaOH, K_2CO_3 and PG aqueous solutions have been measured at lab temperature of 294.82 K with an estimated accuracy of ± 0.1K for concentration range from 0.0 to 8.25mole%. Over the concentration range selected for this study; the agreements with proposed correlations in different literatures are satisfactory. However no experimental data and theoretical correlations available for the thermal conductivity of PG. So the regression model based on Chiquillo correlation has been fitted to experimental data to find the coefficients. With these coefficients the model well fits with experimental data.

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