

# Initial solubility & density evaluation of Non-Aqueous system of amino acid salts for CO<sub>2</sub> capture: potassium proline blended with ethanol and ethylene glycol

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**Abstract.** Amine scrubbing is the state of the art technology for CO<sub>2</sub> capture, and solvent selection can significantly reduce the capital and energy cost of the process. Higher energy requirement for aqueous amine based CO<sub>2</sub> removal process is still a most important downside preventive its industrial deployment. Therefore, in this study, novel non-aqueous based amino acid salt system consisting of potassium proline, ethanol and ethylene glycol has been studied. This work presents initial CO<sub>2</sub> solubility study and important physical properties i.e. density of the studied solvent system. Previous work showed that non-aqueous system of potassium proline and ethanol has good absorption rates and requires lower energy for solvent regeneration. However, during regeneration, solvent loss issues were found due to lower boiling point of the ethanol. Therefore, ethylene glycol was added into current studied system for enhancing the overall boiling point of the system. The good initial CO<sub>2</sub> solubility and low density of studied solvent system offers several advantages as compared to conventional amine solutions.

## 1. Introduction

In chemical absorption processes, amines such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are the most common choice as chemical solvents that have been used industrially for acid gas removal [1]. The main advantage of this technology based on chemical absorption of CO<sub>2</sub> by aqueous amines is its great efficiency; more than 90% of low pressure CO<sub>2</sub> can be captured because of the fast acid-base reaction. However, this process has not yet demonstrated to be suitable for the application to CO<sub>2</sub> removing from large scale commercial power plants (up to 500 ton CO<sub>2</sub>/h), due to energy required for absorbent regeneration [1]. Besides the regeneration energy, other disadvantages are large equipment size [2], solvent volatility [3], solvent toxicity [4], solvent degradation [5]-[7], and high equipment corrosion [8], [9]. In order to make more attractive implementation of the CCS technology to large scale fossil-fuelled power plants, considerable research efforts are undertaken from engineering and chemical point of view, to make the process more economical efficient as well as environmental safe. To achieve this objectives, the absorbent efficiency and its thermal and oxidative stability should be increased, as well as energy costs of the absorbent regeneration should be decreased while maintaining (or enhancing) the other attributes.

To avoid the issues of solvent volatility, toxicity, degradation and corrosion, several researchers have come up with a new class of solvents named as amino acid salts (AASs) [10]-[21]. AASs are the salt form of natural amino acids. They are therefore formed by neutralizing an amino acid compound with an alkali metal hydroxide. Thus, the alkalinity of the amino group is increased, i.e. the amino acid reacts selectively with acid gases such as CO<sub>2</sub>. Due to their ionic nature, both AASs and their



absorption products are conveniently non-volatile [11], [22]. As reported by Eide-haugmo et al. [23], AASs have a high biodegradability and their toxicity is an order of magnitude lower than any of the other alkanolamines, piperazine (PZ) or ammonia. Moreover, Fischer observed that AASs such as potassium N, N-dimethylglycinate, taurate and sarcosinate demonstrated lower degradation rates and less volatile degradation product emissions in comparison to alkanolamines such as MEA and DEA [24]. However, it was recently pointed out that the regeneration energy demand is one of main research area where AASs might have to advance [25]. Evidently, there is a great need for more fundamental research into new chemical solvents.

Earlier, alkanolamines were also used in non-aqueous solutions [26]. An example of this is the Sulfinol process using a mixture of diisopropylamine (DIPA), sulfolane (tetrahydrothiophene dioxide), and water. This process had shown the capability of removing carbonyl sulfide (COS) and mercaptans together with  $H_2S$  and  $CO_2$  [26]. And recently, several researchers have investigated that non-aqueous amine/alcohol solvents offer various improvements such as low binding energy, low heat capacity and high cyclic loading, resulting in a significant decrement of regeneration energy demand of  $CO_2$  absorbed solvents [27]-[29]. Lately, Shen et al. [30] investigated absorption rate of  $CO_2$  in non-aqueous system of potassium proline/ethanol (ProK-EthOH) solution. It was also examined that the ProK-EthOH solvent showed faster absorption rate than aqueous ProK solvent and as well as lower regeneration temperature. However, solvent loss especially ethanol loss during regeneration of solvent was the major issue due to low boiling point of the ethanol need to be addressed for the future studies [30]. Therefore, in this work, ethylene glycol (EG) was mixed with ProK-EthOH solution, so as to increase the boiling point of the azeotropic mixture of EthOH and EG. Moreover, the data on absorption performance of non-aqueous AASs system is scarce in available literature. Here, this work is focused on evaluating the initial  $CO_2$  solubility study of the developed non-aqueous system and evaluating the density of the system.

Knowledge of the physical property such as density of non-aqueous system of ProK-EthOH-EG is essential for process design of gas treating units [31]-[33]. Solution density is important for the mass transfer rate modeling of absorption and regeneration because these properties influence the values of the liquid side mass transfer coefficient [34], [35]. Therefore, in this study, physical properties were measured over the temperature range of 298.15 to 343.15 K and at ProK mass fractions of (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) with the remaining solution containing equal mass fractions of EtOH and EG. In addition, initial  $CO_2$  solubility is investigated for all concentrations into the studied solvent at 5 bar initial pressure.

## 2. Experimental section

### 2.1. Chemicals and solution preparation

The chemicals such as l-proline (Pro), ethanol (EthOH) and ethylene glycol (EG) were provided by Merck Chemicals Germany and potassium hydroxide (KOH) was supplied by Aladdin Reagent China and were used as such. However, the gases such as carbon dioxide ( $CO_2$ ) and nitrogen ( $N_2$ ) were provided by Muscat gases. In order to prepare potassium proline/ethanol (ProK-EthOH) solutions, equimolar mixture of Pro and KOH was added into equal masses of EthOH and EG. All the chemicals were mixed at 400 rpm and atmospheric pressure using a magnetic stirrer for 2 to 3 hrs till a clear and uniform solution was formed. The weight measurements of the chemicals (Pro, KOH, EthOH and EG) were performed using an analytical balance (Mettler Toledo) with a precision of  $\pm 0.1$  mg. All the prepared solutions were preserved in a tightly closed glass container so as to minimize the exposure of air for any contamination. Six different concentrations (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) of ProK were prepared in EthOH-EG solution in terms of mass fraction. All physical properties were measured in a temperature range of 298.15 to 343.15 K, at every 5 K interval.

### 2.2. $CO_2$ absorption experiments

In this study, initial  $CO_2$  solubility tests were performed in order to check the absorption capacity of the newly formulated system of ProK-EthOH-EG. For this purpose, a high pressure solubility cell was used. A brief description of this solubility cell was presented in our previous papers [20], [21].  $CO_2$

solubility in ProK-EthOH-EG system were measured using a pressure drop technique [36] at 313.15 K. The method of CO<sub>2</sub> loading calculation was described briefly in literature [21], [30], [36].

### 2.3. Density measurements

The density of ProK-EthOH-EG solutions was measured at atmospheric pressure using a density meter (Anton Paar DMA 4500 M), with a repeatability of  $\pm 5 \times 10^{-5}$  g.cm<sup>-3</sup> and temperature accuracy of  $\pm 0.01$  K. The equipment works on the theory of oscillation U-tube method [37], [38]. Before any measurements, the cell of the density meter was extensively cleaned with ethanol and water of Millipore quality and dried with a built in air blower. The cleaning and drying procedure was done for the reliability and accuracy of the measured data. The equipment was calibrated for the whole measurement range with water of Millipore quality. In a similar way, the density of the ProK-EthOH-EG solutions was measured. Each density measurement was replicated three times and the calculated uncertainty in the density and temperature data was  $\pm 6 \times 10^{-5}$  g.cm<sup>-3</sup> and  $\pm 0.02$  K respectively.

## 3. Results and discussion

### 3.1. Initial CO<sub>2</sub> solubility test

In this study, initial solubility of ProK-EthOH-EG system was examined at 5 bar initial pressure and at 313.15 K. The obtained solubility data was calculated in terms of CO<sub>2</sub> loading which is mol of CO<sub>2</sub> per mol of solvent used and are presented in Table 1. It was observed from table that as the concentration of ProK in solution increases CO<sub>2</sub> loading decreases. Because with the increase in concentration of ProK, the rate of number of CO<sub>2</sub> absorbed in the solution is less than the rate of number of moles of overall solvent and thus causing the loading to decrease. A similar behaviour in CO<sub>2</sub> loading data with increase in concentration of solvent can be observed in literature also [20], [21], [39], [40].

**Table 1.** Experimental initial CO<sub>2</sub> solubility data in ProK-EthOH-EG solutions at 313.15K.

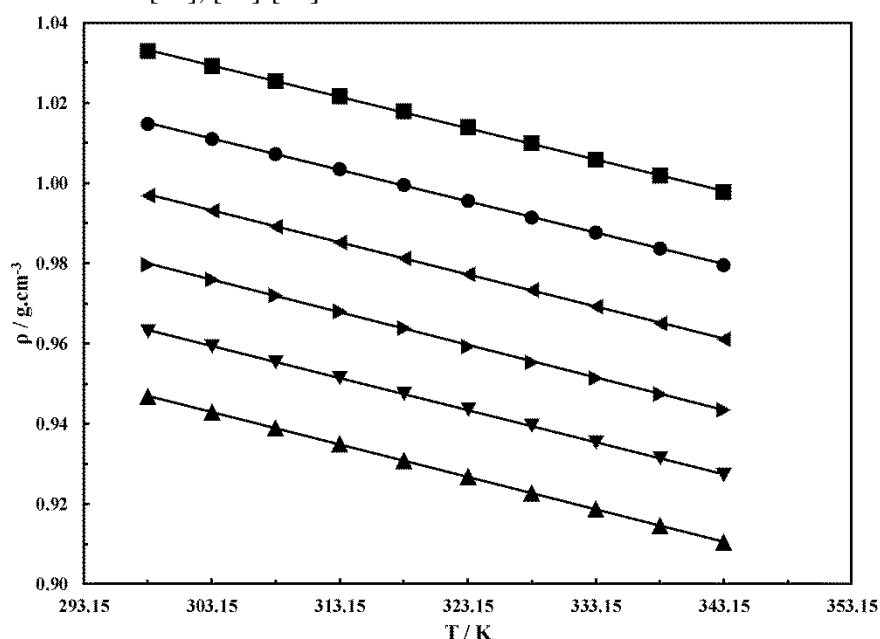
Concentration of ProK in solvent (w)	Pressure (bar)	CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol of solvent)
0.05	3.92	1.456
0.10	3.71	1.310
0.15	3.53	1.196
0.20	3.40	1.079
0.25	3.32	0.965
0.30	3.24	0.871

**Table 2.** Experimental density data of ProK-EthOH-EG solutions at 0.1 MPa.

T/K	density ( $\rho$ /g.cm <sup>-3</sup> )					
	ProK (w)					
	0.05	0.10	0.15	0.20	0.25	0.30
298.15	1.3985	1.4025	1.4066	1.4115	1.4187	1.4225
303.15	1.3972	1.4011	1.4051	1.4103	1.4161	1.4197
308.15	1.3962	1.4003	1.4034	1.4095	1.4143	1.4185
313.15	1.3968	1.4008	1.4038	1.4102	1.4149	1.4190
318.15	1.3983	1.4029	1.4057	1.4123	1.4170	1.4203
323.15	1.4021	1.4062	1.4095	1.4146	1.4208	1.4244
328.15	1.4070	1.4102	1.4135	1.4185	1.4260	1.4299
333.15	1.4109	1.4148	1.4173	1.4229	1.4299	1.4338
338.15	1.4123	1.4176	1.4231	1.4268	1.4314	1.4355
343.15	1.4131	1.4186	1.4242	1.4285	1.4321	1.4363

### 3.2. Density

The experimental density data of ProK-EthOH-EG solutions was measured at several mass fractions (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) and temperature ranging from 298.15 to 343.15 K. The measured density data are reported in Table 2 and the effect of concentration and temperature on density is shown in Fig. 1. It can be observed from Fig. 1 that density increases as the concentration of solvent increases isothermally, hence showing the effect of concentration. Because, as the concentration of ProK molecules increase in the solutions, the intermolecular interactions between ProK and EthOH-EG molecules might increase due to hydrogen bonding and Van der Waals dispersion forces between them, which in turns increases the density. However, density data decrease linearly with the rise in temperature of the solution at any constant concentration. Because at higher temperatures, the spaces between the molecules get increased resulting in the expansion of the solution volume and thus decreasing the density. Similar behaviour in the variation of the density data has been observed in literature also [37], [41]-[43].



**Figure 1.** Plot of experimental density versus temperature for several mass fractions of ProK-EthOH-EG solutions; ▲, 0.05; ▼, 0.10; ►, 0.15; ◄, 0.20; ●, 0.25, ■, 0.30.

### 4. Conclusion

Experimental density and initial CO<sub>2</sub> solubility data of ProK-EthOH-EG solutions were investigated at several concentrations (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) and temperatures (298.15 to 343.15 K). The density data increase with increase in concentration of ProK in the solution, while, an opposite behavior was observed with the rise in temperature of the solution. CO<sub>2</sub> solubility decreases with increase in concentration of ProK in the solution. The data obtained in this work could be useful for the designing of efficient CO<sub>2</sub> absorption system. Additional research on the studied solvent is required in terms of reaction mechanism and absorption rate study for the proper understanding before it can be used on a commercial scale for CO<sub>2</sub> removal processes.

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