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# About benchmarking of amino acid performance for CO<sub>2</sub> absorption

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### Abstract

In this work, we summarize our findings on viscosity and density measurements, absorption energy, and kinetics in pure amino acid aqueous solutions. We also examined mixtures of amino acid salts and tertiary amines, as well as deep eutectic solvents. Viscosity and density play crucial roles in CO2 capture efficiency and flow, making accurate measurements essential for facility sizing and cost calculations. Our research (Delanney et al., 2023) found that aqueous Glycine Potassium (GlyK) solutions have lower viscosity than Glycine Sodium (GlyNa), likely due to sodium ions strengthening the water molecule network. Despite variations in viscosity, these solutions remain effective for CO2 capture. We developed a method to measure enthalpy of absorption with a Setaram C80 micro-calorimeter, revealing that absorption energy relies heavily on loading rates. A blend of MDEA (20% wt.) and K-Lysine (10% wt.) consumed about 20% less heat than MEA (30% wt.), highlighting the importance of solvent formulation. Using a Lewis cell, we studied CO2 absorption kinetics and explored choline-based deep eutectic solvents (DESs) with different water contents. Our findings indicate that adding choline chloride and raising temperature enhance reaction kinetics, suggesting optimized solvent composition and temperature can improve CO2 capture efficiency and offer viable alternatives to conventional amine-based solvents

Keywords: Amino acid, CO2, solvent mixture, physical properties, energy, kinetic

## Introduction

According to the IPCC, the Earth's surface temperature has risen by between  $0.8^{\circ}$ C and  $1.3^{\circ}$ C when comparing the baseline periods of 1850–1900 and 2010–2019. This increase in temperature is directly linked to the rising concentration of greenhouse gases in the atmosphere, primarily due to human activities. Global warming contributes to climate change, which has significant consequences for the planet. Among the various greenhouse gases, carbon dioxide (CO<sub>2</sub>) is the most emitted and is the primary gas responsible for global warming.

To address climate change stemming from global warming, many countries signed the Paris Agreement in 2015, committing to limit the rise in global temperature to below 2°C compared to the 1850–1900 period. One proposed solution is carbon capture and storage (CCS) or carbon capture, utilization, and storage (CCUS). The principle behind

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these technologies is to capture carbon dioxide directly at the source of emissions. A significant portion of industrial processes requires energy in the form of heat, which is mostly generated through the combustion of carbon-based fuels, whether fossil fuels or alternatives. The aim is to capture the  $CO_2$  emitted from the combustion process.

In recent years, researchers have explored the potential of amino acids for capturing carbon dioxide. Several reviews have been published on the effectiveness of amino acid salt solutions in capturing  $CO_2$ . Glycine and lysine, in particular, stands out due to its high absorption rates, solubility, and availability. Additionally, amino-acid salts are resistant to oxidative degradation, have low vapor pressure and can be synthetized in an environmentally-friendly way.

In this work, we present an overview of our results regarding viscosity and density measurement, energy of absorption, and kinetic measurement on pure amino acid aqueous solutions. Moreover, amino-acid salts, by their high reaction kinetics, seem good promoters of tertiary amines. Therefore, mixtures with amino-acid salts and tertiary amines or in deep eutectic solvent are also studied.

#### 1. Viscosity and density determination

The roles of viscosity and density in the effectiveness of capture solvents are well documented. These properties significantly influence the flow of transferred  $CO_2$ . Additionally, estimates of diffusivity and partial transfer constants are often calculated using values of viscosity or density. It is important to note that an increase in viscosity can lead to a loss of mechanical energy due to pressure drops. Therefore, accurately determining viscosity and density is essential for sizing a facility and calculating its operating costs.

Thanks to in-depth bibliographic research, we have developed some correlations that allow us to describe the evolution of viscosity and density with precision (Delanney et al., 2023). The equations and graphs below provide an overview.

$$\eta(Pa \cdot s) = k_5 \cdot (1 + k_6 \cdot w^{0.5} + k_7 \cdot w + k_8 \cdot w^{1.5}) exp\left(\frac{k_9 \cdot (1 + w + k_{10} \cdot w^{1.5} + k_{11} \cdot w^2)}{R \cdot T(K)}\right)$$
$$\rho\left(\frac{kg}{m^3}\right) = k'_1 \times T(K) + k'_2 \times w(mass \ fraction) + k'_3$$





Figure 1. Dynamic viscosity of aqueous GlyK solutions as a function of mass fraction at different temperatures (lines represent model; patterns represent experimental values)  $(\diamondsuit 293,15 \text{ K}; \blacksquare 303,15 \text{ K}; \bigstar 313,15 \text{ K}; \divideontimes 323,$ 15 K)

Figure 2. Dynamic viscosity of aqueous GlyNa solutions as a function of mass fraction at 303.15 K ( $\blacklozenge$  Lee et al.,  $\blacktriangle$  Shaikh et al.,  $\blacksquare$  Chu et al.,  $\bigcirc$  This work).

We have highlighted the lower viscosity of aqueous solutions of GlyK compared with those of GlyNa. Several

explanations can be put forward. Firstly, it is possible that the sodium ion tends to strengthen the network formed by the water molecules, whereas the potassium ion is considered to be neutral with respect to the network. Another explanation is that sodium ions attract water molecules more strongly, resulting in a decrease in free volume and an increase in viscosity. Nevertheless, whatever the concentration, the viscosity of amino acid solutions is not an obstacle to their use in  $CO_2$  capture.

#### 2. Energetic aspects

We have developed a method for measuring enthalpy of absorption that allows measurements to be made for different temperatures, concentrations, pressures and charge rates, based on a Setaram C80 micro-calorimeter. Once again, we carried out numerous measurements on amines, but also on specific amine-based mixtures. The figure below shows some of the results obtained for a mixture of lysinate and MDEA.



Fig. : Exemple of Heat flow (HF) obtained from the DSC per time.  $\neg$  HF for  $\alpha$ =0.25,  $\neg$  HF for  $\alpha$ =0.44.

Fig. Enthalpy of absorption for lysinate Activated MDEA blend

We can see from the initial results that the absorption energy is highly dependent on the loading rate. This information is very important when sizing the process and choosing the cyclic capacity, i.e. the load difference between the unloaded part (desorber outlet) of the process and the loaded part (absorber outlet). Overall, the MDEA 20 % wt. + K-Lys 10 % wt. blend system consumed about 20% less heat in absorption comparatively to MEA 30% wt.. Formulating the solvent is an important stage in developing the capture process. The method developed can be applied to homogeneous solvents and equally to demixing solvents (L/L or S/L).

### 3. Kinetic measurement and Henry constant

The kinetics of  $CO_2$  absorption were studied using a Lewis cell with two independent stirring shafts, which facilitate independent mixing at varying speeds, and is equipped with temperature and pressure sensors. This setup enables automated micro-injections of gas and simplifies analysis by recording pressure and temperature in real time. Analyzing the pressure variations during  $CO_2$  micro-injections in pseudo-first-order regime allows us to determine the kinetic parameters using the following equation:

$$\ln\left(\frac{P_{CO_2,ini}}{P_{CO_2}}\right) = \frac{A \cdot R \cdot T}{V_g} \cdot \frac{\sqrt{k_{ov} \cdot D_{CO_2}}}{He} \cdot t$$

In this part, choline-based deep eutectic solvents (DESs) were prepared with varying water content. Henry's law constant was estimated using the  $N_2O$  analogy, and the kinetics of  $CO_2$  transfer were experimentally determined. A stirred tank reactor, with temperature regulation via a heat transfer fluid, was employed to estimate the solubilities. By combining a mass balance with the Peng-Robinson equation, the solubility of N<sub>2</sub>O was obtained. To validate the measurements of N<sub>2</sub>O solubility in water, we applied the methodology previously established in our laboratory for determining CO<sub>2</sub> solubility in alcohols.



Fig : Henry's law constant of CO2 in ChCl-GlyK-H2O

Fig : Absorption kinetic constant as a function of temperature

The above figure clearly illustrates that both the addition of choline chloride and the increase in temperature for each solution significantly enhance the reaction kinetics. As the temperature rises and choline chloride is introduced, the value of  $k_2$  increases, The data show that optimizing the solvent composition and operational temperature can greatly improve the effectiveness of CO<sub>2</sub> capture.

. The results indicate that these formulations can be a promising alternative to conventional amine-based solvents.

#### Conclusion

The aim of this work is to illustrate the investigations we have carried out into various aspects of  $CO_2$  absorption by pure amino acid solutions or specific formulations. Due to their properties, amino acids deserve to be studied in greater depth, as they could make it possible to remediate  $CO_2$  emissions by making processes more bio-based and less energy-intensive.

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