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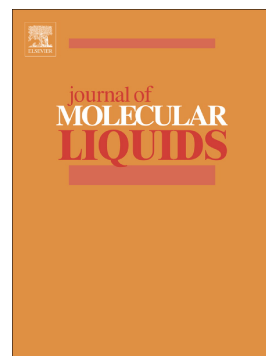
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Carbon Dioxide Absorption into Aqueous Potassium Salt Solutions of Glutamine amino acid

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Abstract

Amino acid salts (AAS) are mentioned as potential solvents for the separation and capture of carbon dioxide (CO_2). This study investigates the aqueous solution of Potassium Glutaminate (K-Glu) solvent from different viewpoints including equilibrium solubility of carbon dioxide varying the concentration and absorption temperature at different pressures, reaction kinetics and mechanism between K-Glu and CO_2, heat of absorption and cyclic absorption and regeneration efficiency. The reaction rate was calculated using the obtained experimental data and quasi first order overall reaction rate is proposed. The successive absorption-desorption preliminary tests showed a negligible drop in CO_2 capture capacity over consecutive cycles through regeneration at 343.15K. The proposed solvent has the advantages of high absorption rate and capacity (compared with monoethanolamine and N-methyldiethanolamine) with interesting aspects such as lower corrosion rate, environmental biening and high resistance against thermal and oxidative degradation covering the shortcomings of conventional amines, which considers it as a potential new solvent.

Keywords: Carbon capture; CO_2 absorption; Amino acid salts; Potassium Glutaminate; Heat of absorption.
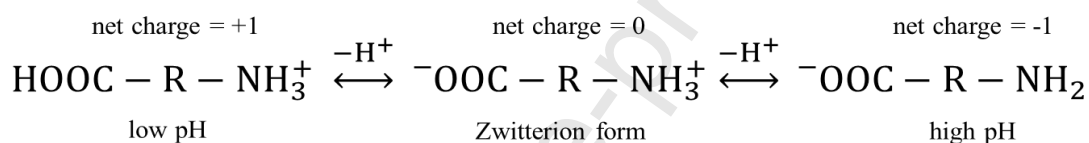
1. Introduction

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Global warming and climate change due to greenhouse gases is the top issue these days that concerns our living on earth; Carbon dioxide is the key gas in greenhouse gases that should be concerned about because it has the most contribution in atmosphere [1-5]. Increasing the CO_2 concentration in the atmosphere is due to different human activities such as deforestation, increasing the utilization of fossil fuels for transportation, buildings and industries and manufacture of cement [6]. Since fossil fuels are used as the most important source of energy, researches seem to be continued to develop appropriate technology for capturing CO_2 with lower costs [7]. Different technologies are developed or under development for carbon capture and sequestration. Among them, physical and chemical absorption seems to be the most practical method due to extensive researches on chemical solvents and their functional applications [8-11]. Although conventional amines such as MEA, DEA and MDEA are commercialized as chemical solvents in industrial scale, but they suffer from a number of disadvantages such as the formation of heat stable salts, inadequate cyclic CO_2 loading capacity, high regeneration energy, corrosion of equipment and flow lines, foaming, and etc. [12]. For this reason, it is suggested to search for an appropriate alternative for amines or improving the amine-based solvent with additives in order to overcome some of these shortcomings. Recently, amino acids and amino acid salts have been attracted much attention due to their particular properties such as high CO_2 loading, lower corrosion rate, environmentally friendly and high resistance against thermal and oxidative degradation [13, 14]. Amino acid salts have a lower volatility due to their ionic nature and it reduces the absorbent loss during the regeneration. The main disadvantage of amino acid salts is probably their price and molecular weight. High molecular weight cause an increase in absorber size especially when CO_2 fraction is high as in the case of biogas [15].

2

Amino acids are known as organic compounds comprising of amine groups (-NH$_2$) in addition to carboxyl (-COOH) functional groups, together with a specific side chain (R group). Scheme 1 shows different equilibriums in an aqueous solution of amino acid. As shown, a neutral molecule (zwitterion) exists in a bipolar form in solution because of proton transfer from carboxylic group to amine group. Adding a base to the amino acid solution can remove a proton from the ammonium group and leaves the molecule with a negative net charge. Amino acid salts that have been used for the absorption of carbon dioxide are formed from neutralization of amino acids with alkali metal hydroxides like LiOH, NaOH or KOH [8, 16]. (Scheme 2)
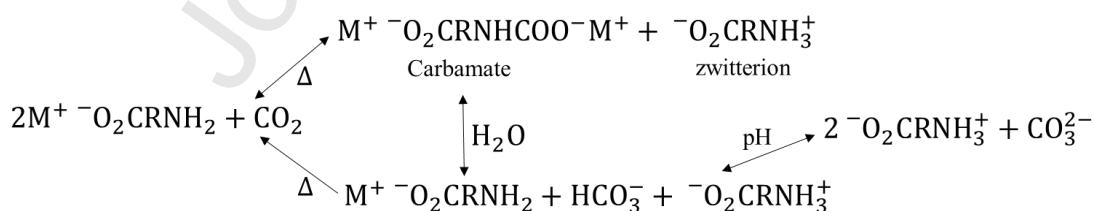
$$\underset{\text{low pH}}{\overset{\text{net charge} = +1}{HOOC - R - NH_3^+}} \overset{-H^+}{\longleftrightarrow} \underset{\text{Zwitterion form}}{\overset{\text{net charge} = 0}{^-OOC - R - NH_3^+}} \overset{-H^+}{\longleftrightarrow} \underset{\text{high pH}}{\overset{\text{net charge} = -1}{^-OOC - R - NH_2}}$$

Scheme 1: Equilibrium equations for aqueous form of amino acid.

$$^-OOC - R - NH_3^+ + M^+OH^- \rightarrow M^+ \, ^-OOC - R - NH_2 + H_2O$$
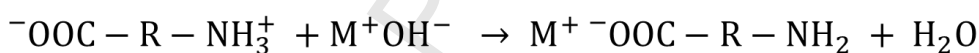
Scheme 2: Amino acid neutralization to amino acid salt.

Amino acid salts react with CO$_2$ like alkanolamines due to the similar functional groups (amine). The equilibrium reactions involved in carbon dioxide chemical absorption in an aqueous solution of amino acid salt are as follow:

$$
\begin{array}{c}
\underset{\text{Carbamate}}{M^+ \, ^-O_2CRNHCOO^-M^+ + \, ^-O_2CRNH_3^+ \, \text{(zwitterion)}} \\
\Delta \nwarrow \qquad \uparrow H_2O \qquad \overset{pH}{\nearrow} 2 \, ^-O_2CRNH_3^+ + CO_3^{2-} \\
2M^+ \, ^-O_2CRNH_2 + CO_2 \\
\Delta \searrow \; M^+ \, ^-O_2CRNH_2 + HCO_3^- + \, ^-O_2CRNH_3^+
\end{array}
$$

Scheme 3: The mechanism of CO$_2$ absorption in amino acid salts.

According to Scheme 3, after the absorption of carbon dioxide, the formed carbamate hydrolyzes and carbonate or bicarbonate could be formed depending upon the pH solution.

The higher the alkalinity of the amino acid salt solution, the greater the CO_2 absorption and it causes the reaction environment to be more acidic after CO_2 absorption [16, 17].

So far, different studies have investigated some of amino acid salts like Glycine, Alanine, Lysine, Arginine, Proline and etc. Recently, Guo et al. [18] examined the absorption performance of water-lean solutions of Potassium Lysinate in addition to Potassium Prolinate. Their study showed lower absorption rate of CO_2 due to the high viscosity of the solutions. Hamzehie et al. [19] measured the CO_2 solubility in aqueous solutions of Potassium Glycinate in various mass fractions including 0.01, 0.04 and 0.1 at different absorption temperatures in the range of 293.15-323.15 K and CO_2 partial pressures of 2.9-1382.4 kPa. The attained results showed high resistance of proposed amino acid salt against degradation in the presence of oxygen compared to conventional alkanolamines. Shen et al. [20] showed that the CO_2 absorption capacity of K-Lys is higher than of conventional alkanolamines like MEA. The investigation of CO_2 solubility in aqueous solution of 10wt.% Sodium β-Alaninate at high pressure revealed excessive absorption capacity of this solvent (higher than 1 mole CO_2/mole AAS) at 303.15 K [21]. Mohsin et al. [22] studied the mixture of Glycine and 3-dimethylaminopropylamine using the concentration range of 0.1-2.0 M. It was found that the net absorbed CO_2 is increased by absorbent concentration. The VLE data of two potassium salts including Glycine and Taurine was attained by Aldenkamp et al. [23] for two concentrations of 1 and 1.8 mole/kg and temperature range of 313-393 K. According to the obtained results, the loading of CO_2 in Potassium Taurate solution was higher than Potassium Glycinate.The equilibrium solubility of carbon dioxide in Potassium Asparaginate and Potassium Glutaminate aqueous solutions were investigated at different temperatures and equilibrium pressures [24]. The obtained results showed that absorption capacity of Potassium Glutaminate was higher than that of Potassium Asparaginate. In addition, they proposed Potassium

4

Glutaminate as a potential CO_2 solvent for further investigations. However, the complete investigation of K-Glu amino acid salt including absorption rate, capacity at moderate concentrations, heat of absorption and performance of solvent in successive regeneration cycles were not investigated at all.
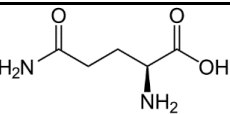
Briefly, the search for new solvents with good CO_2 absorption rate and adequate absorption capacity is in progress to prevail the inadequacies of conventional MEA and MDEA based technologies. Accordingly, the absorption-desorption efficiency of Potassium Glutaminate solution was examined at different operating conditions. The effects of K-Glu concentration, absorption temperature and equilibrium pressure on the kinetics of CO_2 absorption were studied in detail. Furthermore, the zwitterion mechanism was used to describe the reaction chemistry.

2. Material and methods

2.1. Chemicals and apparatus

L-Glutamine and potassium hydroxide were purchased from Merck Company and used as received without further purification. Different solutions were prepared by means of distilled water and carbon dioxide with purity of 99.9% was used in absorption tests. The physical properties and structure of L-Glutamine are represented in Table 1.

Table 1: Properties of the amino acid used [25].

Component	Structure	M_w (g/mole)	Solubility (gr/kg_{H_2O})	pK$_a$ (-COOH)	pK$_b$ (-NH$_2$)	Isoelectric Point	LD50 (mg/kg)
L-Glutamine		146.15	42	2.18	9.00	5.59	7500

Potassium Glutaminate solution was prepared with the addition of an equimolar amount of KOH to the aqueous solution of Glutaminate and hence the carboxylic group neutralized. In this study, a low pressure solubility cell was applied to perform the solubility

experiments as demonstrated schematically in Fig. 1. The solubility cell with the effective volume of 350ml was equipped with a magnetic stirrer to homogenously stir the absorption media. The temperature of whole setup was regulated using an accurate water bath to control the absorption temperature. Before each experimental test, the vessel was purged with nitrogen and then was vacuumed to remove all unwanted gases inside. Afterwards, the pure CO_2 was injected into the equilibrium cell through a transfer vessel and left it to set the temperature to the required test condition. Then, the solvent was injected by means of a syringe pump, the stirrer turned on with the rate of 1000 rpm and the data of temperature and pressure were recorded accurately and sent to a computer by means of the data logger during the absorption process. In addition, the pH value of solution before and after absorption was determined using a Metrohm pH meter.
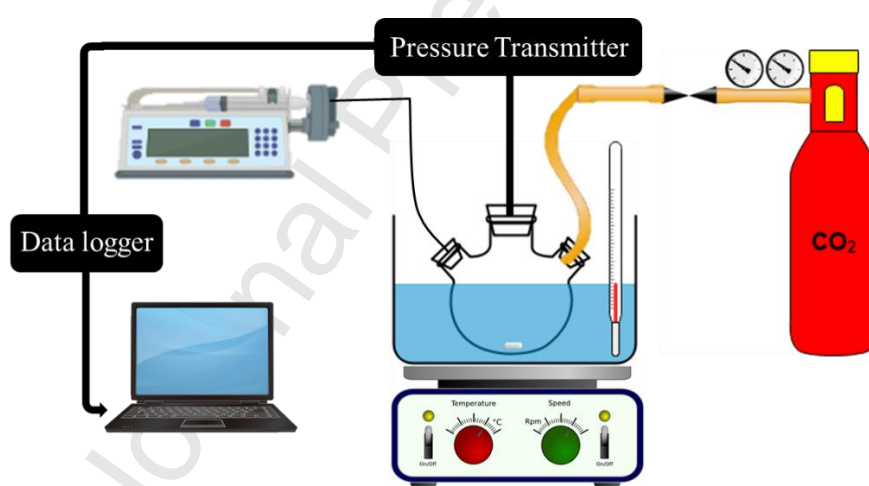

Fig. 1: The schematic of experimental setup.

The cyclic absorption-desorption experiments were performed through the saturation of solvent with carbon dioxide at acquired absorption temperature, followed by the regeneration at 343.15 K during three successive cycles.

2.2. Theoretical background

The search for finding the reaction rate and reaction rate parameters could significantly help us to preliminary comparing different amino acid salt with conventional amines and is

6

vital application for industrialization of such solvents. The reaction between amino acid salts and carbon dioxide could be discussed on the basis of zwitterion mechanism and could be applied in order to model the CO_2 absorption in the aqueous solutions of different alkanolamines and various amino acid salts [26-28]. In this mechanism, the zwitterion is formed as intermediate according to the deprotonating through the reaction with water hydroxyl or amino groups of amino acid salts resulting in the formation of carbamate (Schematic 1-3). Assuming steady-state conditions for the concentration of zwitterion ion, the reaction rate could be attained using the initial slope of pressure versus time data. Previous studies showed that the overall reaction rate of some amino acid salts obey first order reaction rate with respect to amino acid salt [26-31].

In order to calculate the total amount of CO_2 in the absorption cell and the solution, the same procedure is used as in the literatures [32-34]:

$$n_{CO2} = \frac{P_{CO2}V}{RT} \tag{1}$$

$$n_{CO2.final} = \frac{(P_{CO2.final} - P_{vapor})(V - V_{absorbent})}{RT} \tag{2}$$

In equation (1), P_{CO2} is the partial pressure of CO_2 in the cell, V is the total volume of cell and n_{CO2} is the total amount of CO_2 before absorption. After the absorption is completed, total amount of CO_2 is calculated according to equation (2), $P_{CO2.final}$ and P_{vapor} are the partial pressure of CO_2 at equilibrium and vapor pressure of solution, respectively. In addition, the $V_{absorbent}$ is the volume of injected solution. Afterthought, the absorption capacity can be calculated using the following equation:

$$\alpha = \frac{(n_{CO2} - n_{CO2.final})}{n_{AAS}} \tag{3}$$

While n_{AAS} is the moles of AAS in the solution.

Interaction energy or heat of absorption is known as the most important parameter, that presents a clear suggestion of complex formation [34, 35]. The heat of absorption could be

calculated using VLE data of K-Glu aqueous solution at the temperature range of 293.15-
313.15 K by means of a simplified Gibbs-Helmholtz equation as follows:

$$[\frac{\partial \ln(P_{CO_2})}{\partial(1/T)}]_\alpha = {-\Delta H_{abs}}/{R} \tag{4}$$

The absorption enthalpy of K-Glu solution was obtained by plotting $\ln P_{CO_2}$ against $\frac{1}{T}$
according to equation 4 at constant absorption capacity followed by finding the line slope
for each capacity [33].

3. Results and discussion

3.1. Reliability test

To prove the experimental method and absorption system applied in this paper, a series of
experiments were conducted on the solubility of CO_2 in aqueous solution of MDEA (2.5M)
at 313.15K. The attained experimental data are compared with presented data in literatures
[36, 37] at different equilibrium pressures indicated in Fig. 2. It could be observed that the
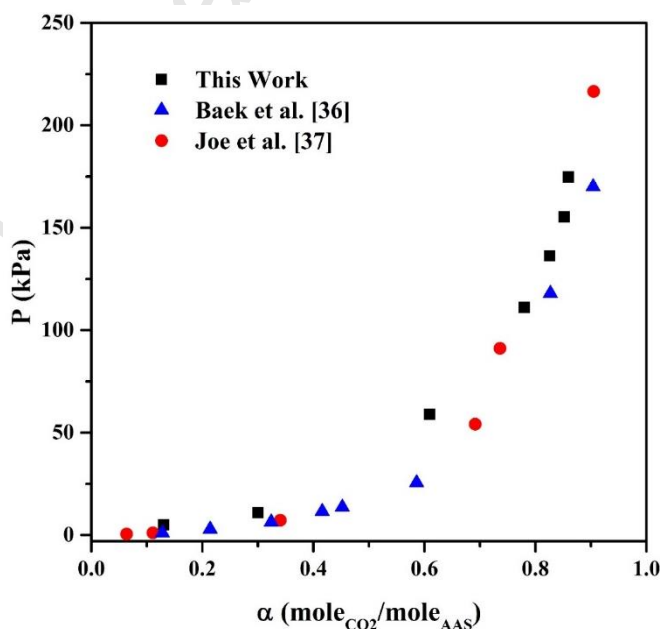obtained results are in suitable arrangement with previous studies.

Fig. 2: The comparison of CO_2 solubility of MDEA and presented data in literatures.

3.2. Equilibrium CO_2 Solubility

8

The CO_2 solubility data presents quantitative criteria to compare the performance of absorbents and helps the process designer to select the adequate solvent for industrial process. In this regard, the physical property, absorption rate, capacity and desorption characteristics of solvents are measured experimentally and recorded in the literatures. For this purpose, the CO_2 solubility in aqueous solution of Potassium Glutaminate is experimented in a batch reactor at different concentrations, absorption temperature and equilibrium pressures. Since the low temperature is the favorable condition in the CO_2 absorption process by amines, the tests are designed in temperature range 293-313K.

The CO_2 solubility data of Potassium Glutaminate at different weight percentages of 2, 6 and 10, different absorption temperatures 293.15, 303.15 and 313.15K and equilibrium pressure up to 220kPa are indicated in Table 2 and graphically represented in Fig. 3a-f. It could be understood that at the similar absorption temperature and CO_2 partial pressure, the CO_2 molar loading depends significantly on the concentration of amino acid salt. It reveals that increasing the weight percentage of amino acid salt has negative effect on the molar loading of carbon dioxide, while higher CO_2 could be loaded in constant volume of solution at higher AAS concentrations. For instance, the CO_2 molar loading of 1.59 and CO_2 absorption per solution weight of about 4.7 were obtained at 293.15 K for the solutions with 2 and 10 wt.% AAS, respectively. This capacity is much higher than that of conventional alkanolamines such as MEA, DEA and MDEA solutions [9, 38].

It can be seen that at the same temperature and CO_2 partial pressure, the CO_2 molar loading per mole of amino acid is decreased with increasing the concentration of amino acid salt in solution, which is agreement with other previous studies [18, 21]. On the other hand, for better understanding the effectiveness of solution for the absorption of carbon dioxide, the CO_2 molar loading per kg of solution could be helpful. The results show increase in net loading of solution by means of increasing the amino acid weight percentage. Higher

9

loading of carbon dioxide per kg of solvent could significantly reduce the solvent circulation price and contactor size. According to the exothermic nature of CO_2 absorption, the loading is decreased by increasing the temperature in all concentrations and partial pressures.

Table 2: Solubility ($\alpha \left(\frac{mol\ CO_2}{mol\ AAS}\right)$ and $\alpha'(\frac{mol\ CO_2}{kg\ solution}$)) of carbon dioxide in K-Glu solution[a].

	2wt.%			6wt.%			10wt.%		
P_{CO_2}(kPa)	$\propto$	$\propto'$	P_{CO_2}(kPa)	$\propto$	$\propto'$	P_{CO_2}(kPa)	$\propto$	$\propto'$
T=293.15K								
20.31	0.616	0.662	21.56	0.526	1.665	21.56	0.412	2.108
29.37	0.820	0.881	32.81	0.750	2.370	28.43	0.573	2.935
39.68	0.915	0.984	83.75	0.926	2.930	42.81	0.694	3.554
84.06	1.216	1.307	145.94	1.020	3.222	70.94	0.766	3.923
155.94	1.445	1.557	206.25	1.024	3.239	135.00	0.840	4.300
216.56	1.590	1.710	-	-	-	193.75	0.920	4.701
T=303.15K								
21.87	0.483	0.520	22.50	0.364	1.150	23.12	0.400	2.041
31.25	0.786	0.845	29.69	0.610	1.924	29.37	0.546	2.798
48.44	0.950	1.022	43.44	0.751	2.373	45.31	0.681	3.485
87.50	1.134	1.220	87.50	0.872	2.758	73.44	0.734	3.758
158.12	1.351	1.453	146.87	0.986	3.116	137.81	0.806	4.125
218.75	1.492	1.604	207.19	1.045	3.306	196.25	0.865	4.427
T=313.15K								
26.56	0.638	0.686	25.62	0.450	1.420	25.31	0.311	1.595
37.19	0.803	0.863	29.69	0.551	1.741	33.12	0.514	2.631
51.87	0.933	1.003	47.81	0.690	2.179	51.25	0.622	3.184
91.25	1.073	1.153	90.62	0.832	2.630	76.87	0.687	3.520
161.56	1.282	1.378	149.68	0.930	2.934	140.62	0.772	3.953
221.87	1.417	1.523	209.37	0.998	3.157	200.00	0.822	4.209

[a] The standard uncertainties (u) are u(T) =0.1 K, u(α) = 0.005 $\frac{mol\ CO_2}{mol\ AAS}$, u($\alpha'$) = 0.005 $\frac{mol\ CO_2}{kg\ solution}$, u($P_{CO2}$) = 2.00 kPa
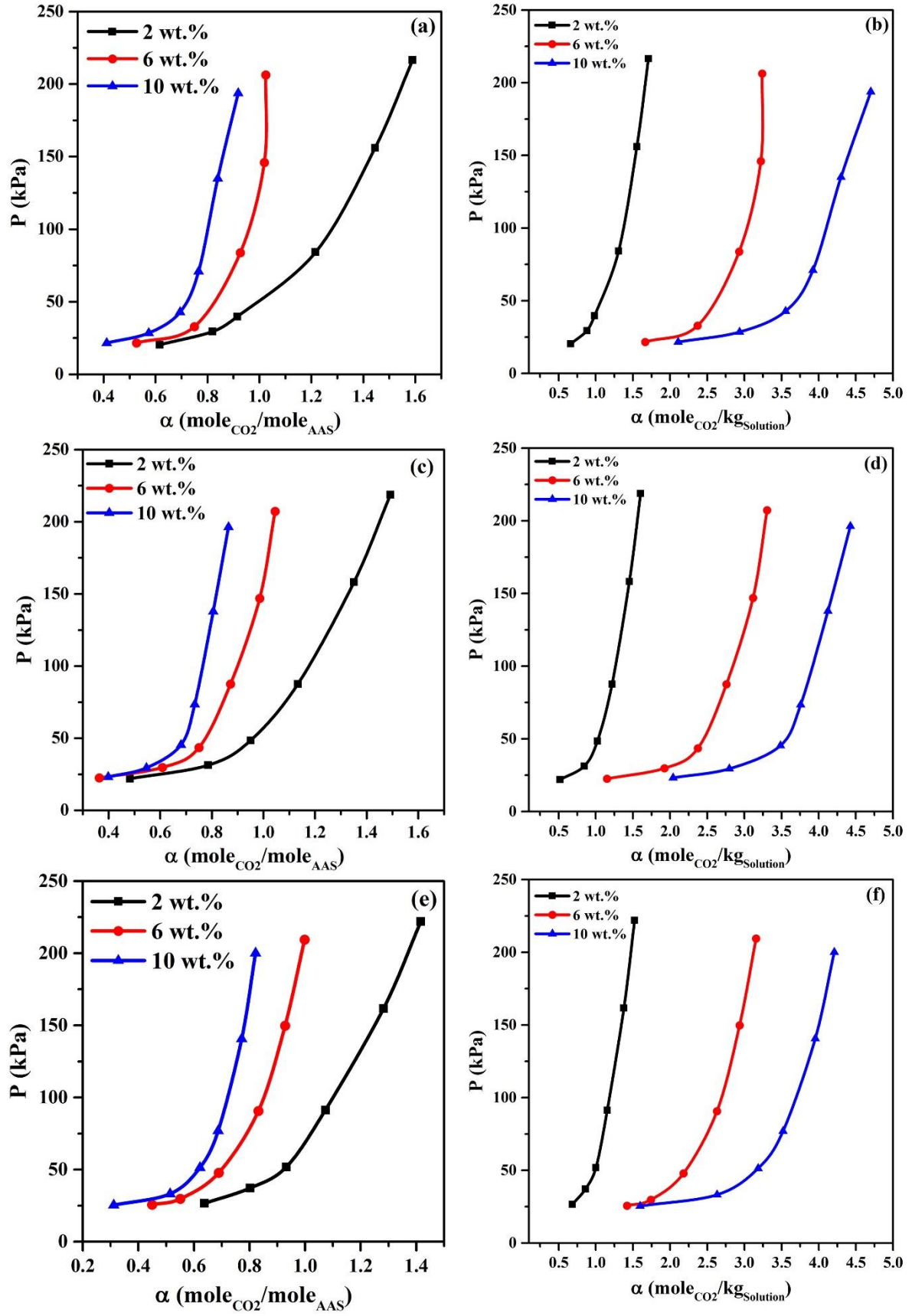
Fig. 3: The effect of amino acid salt weight percentage (2, 6 and 10 wt.%) on the solubility (mole $_{CO2}$/mole $_{AAS}$) of CO_2 at: (a, b) 293.15 K, (c ,d) 303.15 K and (e, f) 313.15 K.

12

In addition to solubility data of carbon dioxide at different temperatures and equilibrium pressures, the trend of pH can confirm the attained data. Fig. 4a-c show that at a constant molar loading, increasing in amino acid salt concentration reduces the pH of solution at equilibrium conditions. In addition to lower pH value, the deference in pH of lean and rich solution (ΔpH) shows a significantly change in pH for the solutions with higher AAS loading, whilst, the initial pH of solution increases with concentration. This phenomenon belongs to the increment in CO_2 loading with increasing of AAS concentration. On the other hand, the slope of ΔpH with loading is decreased, that is related to the reduction of CO_2 loading at higher equilibrium pressures. Generally, the ΔpH is increased with CO_2 loading while the slope of ΔpH versus CO_2 molar capacity is increased with AAS concentration and slightly decreased with temperature.

The amino group in K-Glu is known as primary amine that has the opportunity for the formation of carbamate during the absorption of carbon dioxide. In addition, the basic aliphatic e-amino group in the side chain structure of glutamine could expose a positive charge with increasing the loading of carbon dioxide. The as mentioned positive charge might contribute in H-bond for the associating of water that favors to deprotonate the CO_2-amino acid complex and facilitate the formation of carbamate. Furthermore, the deprotonated e-amino group could absorb carbon dioxide as a primary amine group at low loadings and high pH [20]. The formed carbamate might be hydrolyzed to bicarbonate and deprotonated amino group in the appropriate pH range [39, 40]. Thus, the higher absorption capacity of K-Glu compared to some other amino acids and conventional alkanolamines such as MEA and MDEA (results indicated in Fig. 6) might be due to the presence of two nitrogen based groups, where one acts as a base for proton acceptance and the other for the formation of carbamate [20].
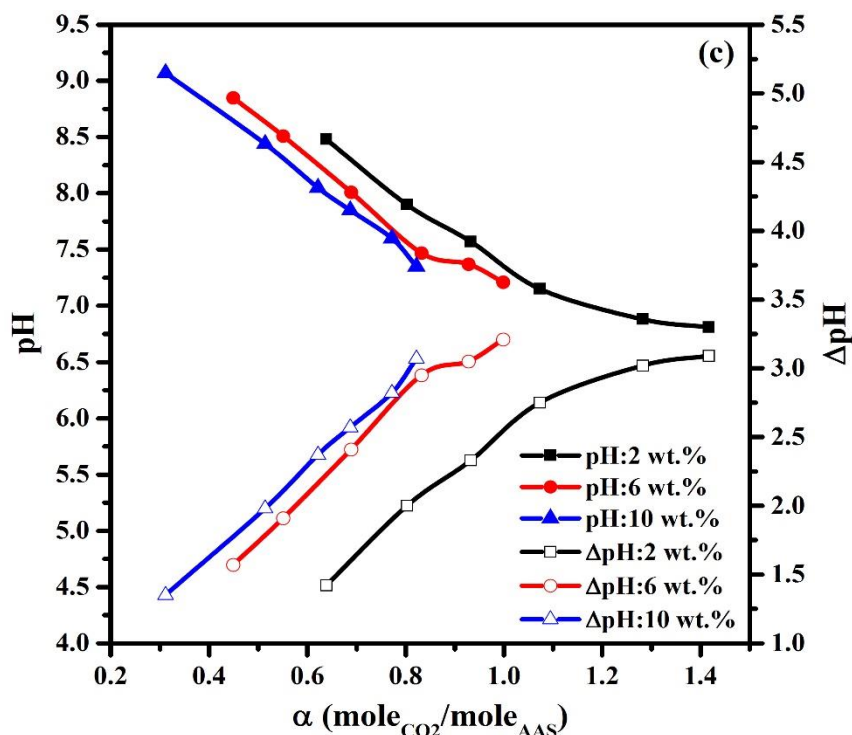
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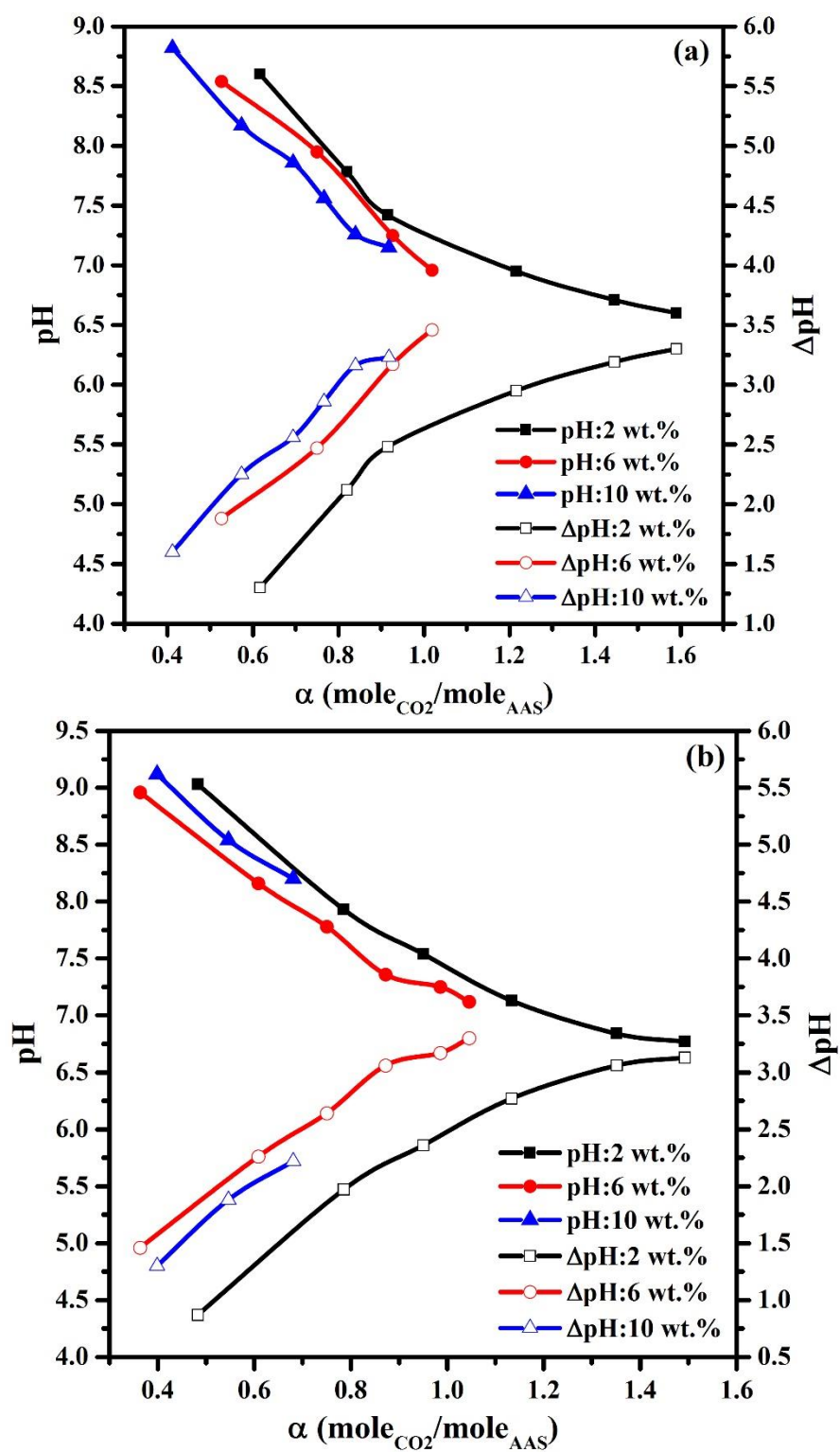
Fig. 4: the pH of solution at equilibrium versus different loadings for the absorption temperatures of: (a) 293.15 K, (b) 303.15 K and (c) 313.15 K.

3.2. CO$_2$ Absorption Rate

The data of absorption rate for different solutions at various operating conditions could be helpful in column design and comparison with conventional absorbers. The absorption rate of carbon dioxide for the solutions with different concentrations at 293.15-313.15 k are presented in Fig. 5. As indicated in this figure, the absorption temperature revealed a significant influence on the saturation time of solvents for all concentrations. Increasing the absorption temperature improves the absorption rate but exposed negative effect on equilibrium capacity for all concentrations. The highest loading amount of 1.590 (mole CO$_2$/mole AAS) was obtained using a 2 wt.% solution of K-Glu at 293.15 K with the final absorption time of 600 s.
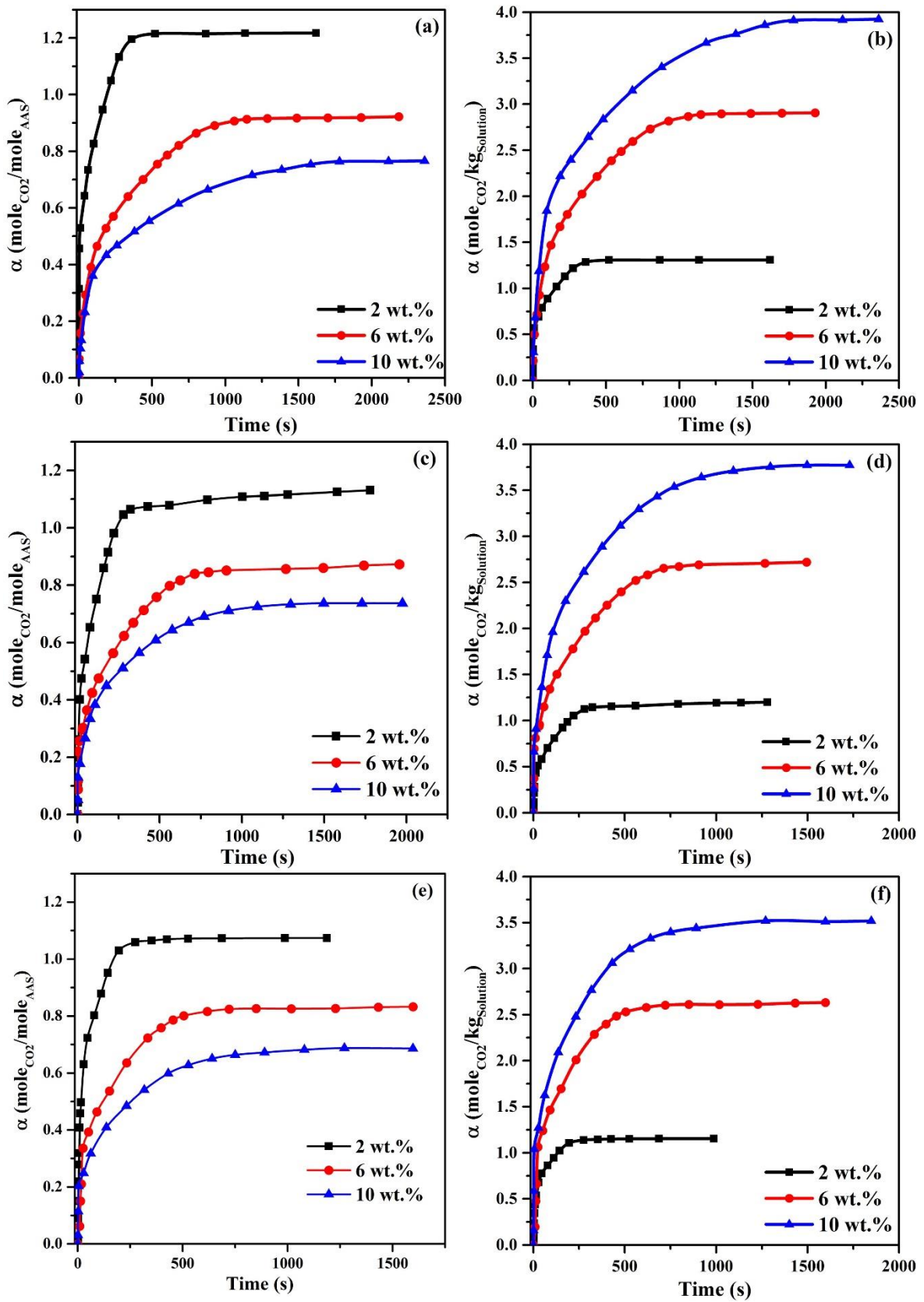
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Fig. 5: CO_2 absorption rate in K-Glu solution at 100 kPa for temperatures of (a, b) 293.15 K (c, d) 303.15 K and (e, f) 313.15 K.

16

According to Fig. 5, the absorption rate of CO_2 in Potassium Glutaminate solution can be calculated using the initial slope of each diagram at different temperatures and concentrations for $t_{0.2}$ ($t_{0.2}$ means the absorption time that 20% of the final loading is achieved) [41]. The comparison of absorption rates represented in Table 3 shows that increasing the absorption temperature and concentration improves the absorption rate.

Table 3: Reaction rates of K-Glu with CO_2 for different concentrations at three absorption temperatures ($P_{initial}$=100 kPa).

T (K)	Reaction rate: $-r_{CO_2} \times 10^4$ (mole CO_2 /L.S)		
	2 wt.%	6 wt.%	10 wt.%
293.15	1.84	2.28	2.71
303.15	2.06	2.93	3.80
313.15	2.28	3.58	4.34

In order to investigate the industrial applicability and competitiveness of proposed solvent, the comparison of a 10 wt.% K-Glu aqueous solution with MEA and MDEA solutions at different concentrations are demonstrated in Fig. 6. This figure shows that the initial absorption rate of K-Glu solution is in the same order of MEA solution, while the loading capacity is to some extent higher than that of MDEA. Therefore, this solvent has both of the most import advantages of MEA and MDEA conventional solvents (high absorption rate and capacity) along with the general aspects such as lower corrosion rate, environmental friendly and high resistance against thermal and oxidative degradation. It can reduce the number of stages of absorption column along with the reduction in circulating solvent, which reduces the capital and operating costs significantly.
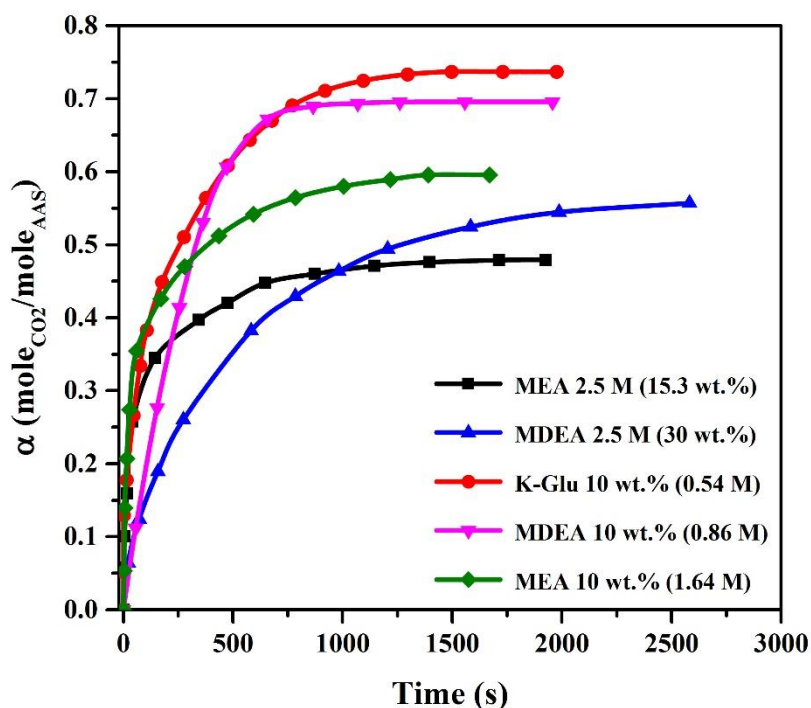
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Fig. 6: Comparison of absorption rate of K-Glu with amines at 303.15 K and
initial pressure of 100 kPa.

3.3. Heat of absorption

The heat of CO_2 absorption is known as a key parameter that is directly associated to the regeneration energy requirement. Thus, heat of absorption is calculated using Clausius-Clapeyron equation discussed in the previous section for different concentrations of aqueous K-Glu solution. The heat of CO_2 absorption for a range of CO_2 loading at different K-Glu concentrations and pure water are demonstrated in Fig. 7. The heat of absorption is increased with increasing the absorber concentration dedicated to the increasing in chemical reaction undergoing in a constant volume of solution. In fact, increasing the AAS concentration increases the ratio of chemisorption compared to physisorption, which has a higher effect at higher AAS contents. In addition, the heat of absorption is increased with CO_2 loading for all concentrations, which is in agreement for the calculated values from the data in the literature [24]. The highest and lowest values for the heat of reaction were attained for MEA (82.39 kJ/mole CO_2) and MDEA (44.65 kJ/mole CO_2), correspondingly.

18
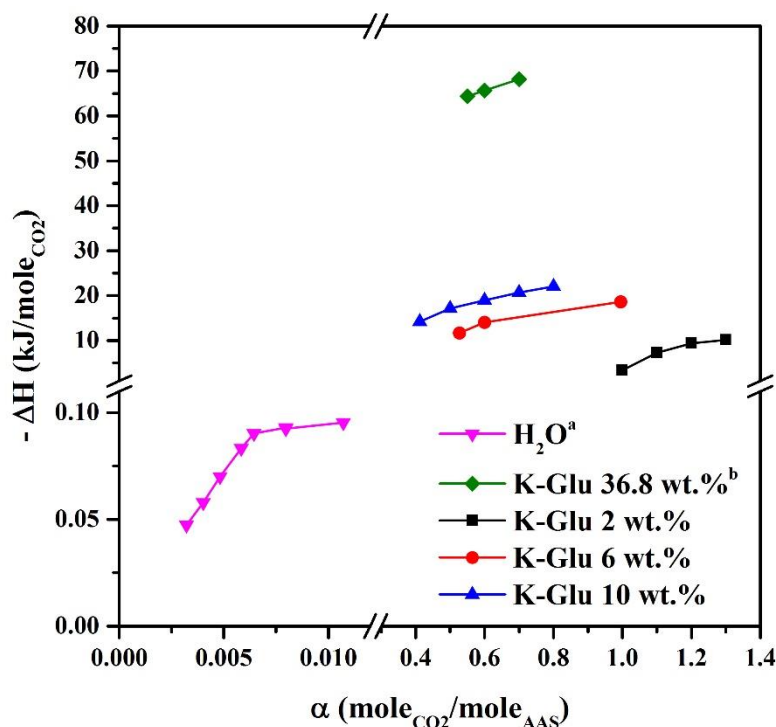
[a] Data obtained for pure water at 2 MPa [42].
[b] Calculated heat of absorption using Clausius-Clapeyron equation from data of [24].

Fig. 7: Heat of CO_2 absorption in aqueous K-Glu solution at different concentrations.

3.4. Cyclic Performance

In this section, the cyclic performance of prepared solutions are compared through continuous absorption and desorption processes. The cyclic performance could be helpful to investigate the effective loading and deactivation of absorbents during the continuous cycles. In this research, the pressure changes due to absorption using each sample is examined through the saturation of solvent with carbon dioxide at different absorption temperatures of 293.15, 303.15 and 313.15 K and subsequently regeneration at 343.15K during three successive cycles. Fig. 8 represents the pressure change in consecutive cycles for the solvents with different concentrations at three absorption temperatures. In general, there is not a considerable difference between the cyclic loading of base and promoted solutions especially at lower concentrations and absorption temperatures. At higher absorption temperature (313.15 K), a slightly loss of absorption capacity occurs for the

19

solvent with 10 wt.% K-Glu that might be due to the change in solvent concentration during the absorption cycles.
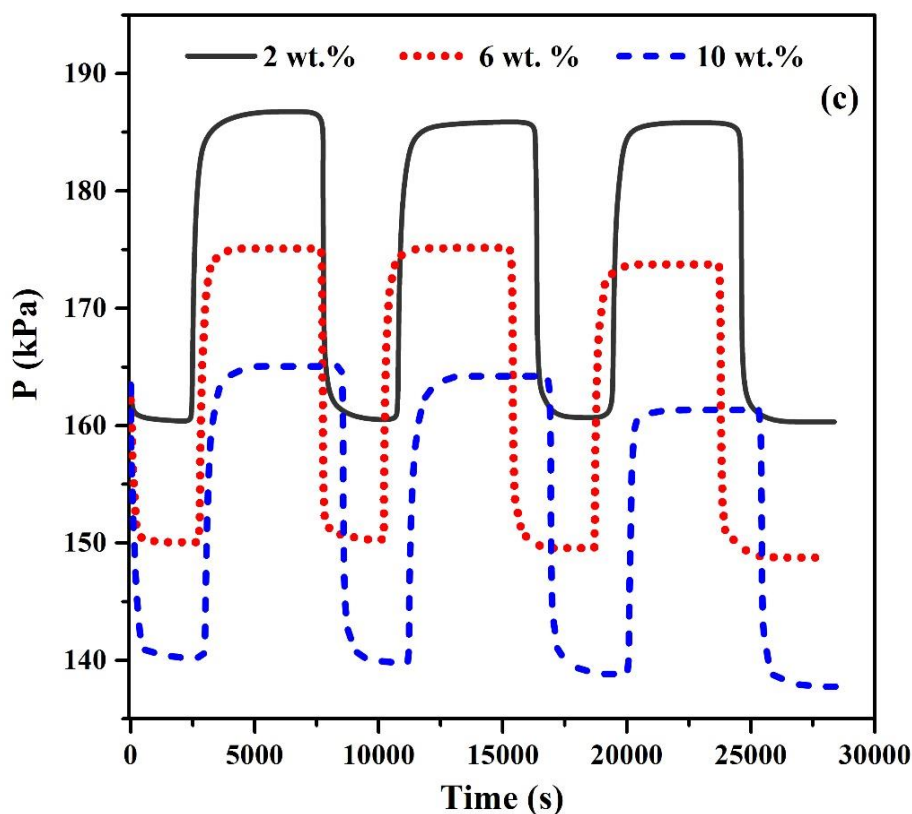

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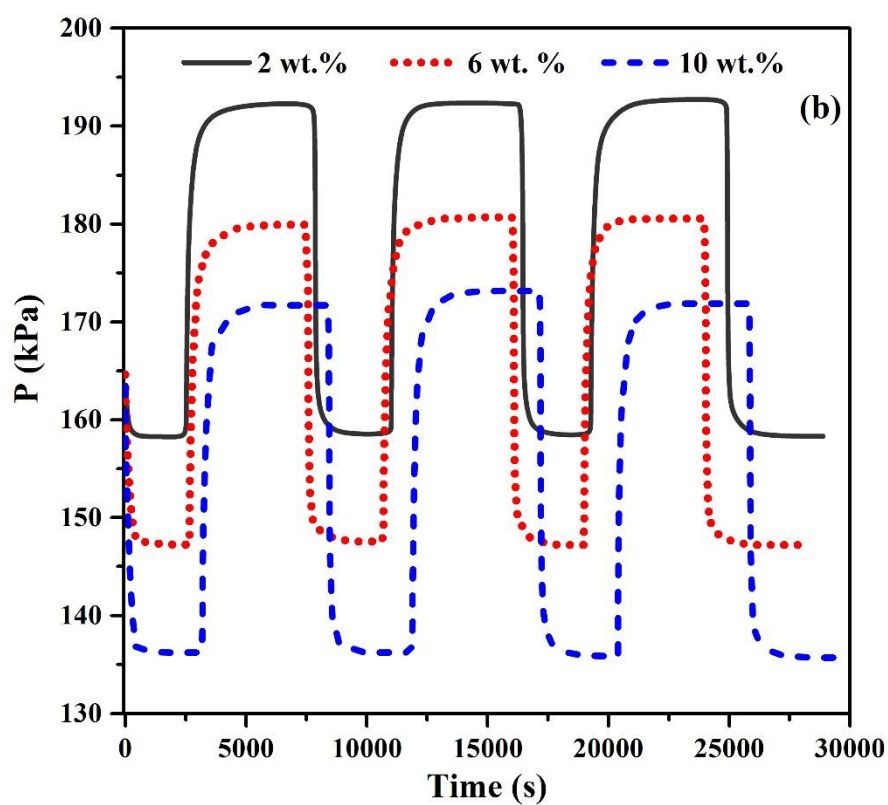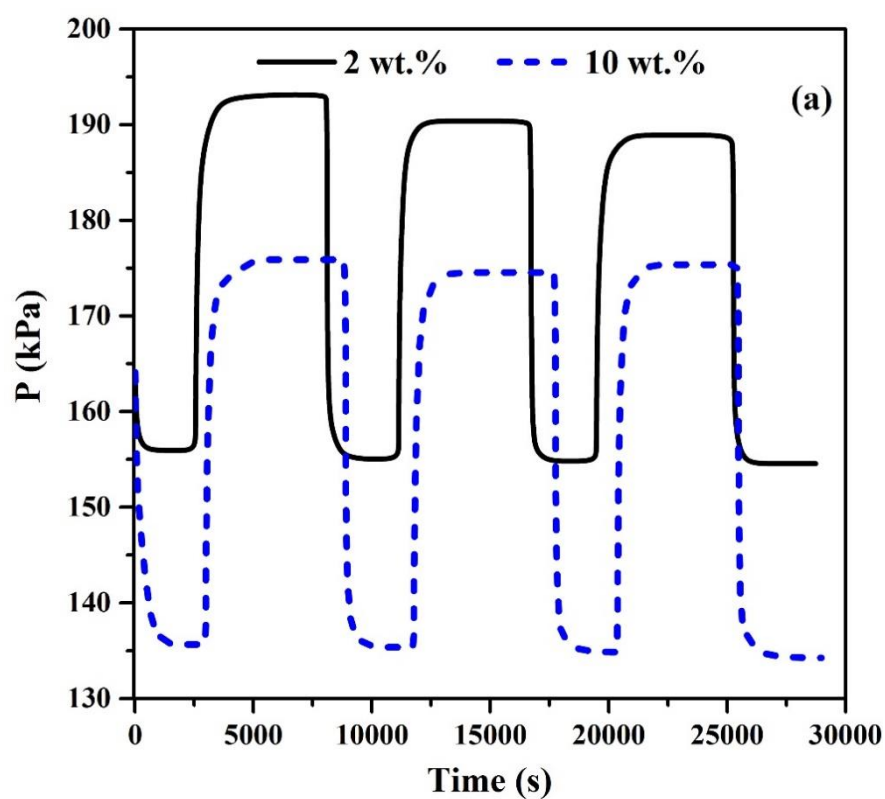
Fig. 8: Thermal regeneration cycles of aqueous K-Glu at different concentrations and for temperatures of (a) 293.15 K, (b) 303.15 K and (c) 313.15 K

Accordingly, the comparable absorption capacity and rate with MDEA and MEA along with good regeneration efficiency, suggest the new K-Glu solvent as an alternative for industrial applications.

4. Conclusion

In the present study, the potential of potassium Glutaminate aqueous solution was investigated for the absorption of carbon dioxide. The equilibrium absorption results revealed high absorption capacity of proposed solvent at different temperatures and concentrations in a range of low equilibrium pressures. Additionally, the low heat of absorption compared to conventional amines suggest considerably lower regeneration energy, which directly affects the economy of unit. Various interesting aspects of this solvent such as high absorption rate and capacity, low heat of absorption, minor corrosion

21

rate, environmentally friendly, not formation of heat stable salts and high resistance against thermal and oxidative degradation compared to conventional amines make it as a potential solvent for CO_2 capture. Consequently, from the perspective of kinetics, equilibrium, energy and regeneration, K-Glu is considered to be an appropriate solvent for CO_2 absorption.

References

[1]   I. Alirezaei, A. Hafizi, M. R. Rahimpour, and S. Raeissi, "Application of zirconium modified Cu-based oxygen carrier in chemical looping reforming," *Journal of CO2 Utilization,* vol. 14, pp. 112-121, 2016/06/01/ 2016.

[2]   M. Mofarahi, Y. Khojasteh, H. Khaledi, and A. Farahnak, "Design of CO2 absorption plant for recovery of CO2 from flue gases of gas turbine," *Energy,* vol. 33, no. 8, pp. 1311-1319, 2008.

[3]   T. Altamash *et al.*, "Gas solubility and rheological behavior study of betaine and alanine based natural deep eutectic solvents (NADES)," *Journal of Molecular Liquids,* vol. 256, pp. 286-295, 2018.

[4]   J.-G. Lu *et al.*, "Property of diethanolamine glycinate ionic liquid and its performance for CO2 capture," *Journal of Molecular Liquids,* vol. 211, pp. 1-6, 2015.

[5]   I. Alirezaei, A. Hafizi, and M. R. Rahimpour, "Syngas production in chemical looping reforming process over ZrO2 promoted Mn-based catalyst," *Journal of CO2 Utilization,* vol. 23, pp. 105-116, 2018/01/01/ 2018.

[6]   D. Fu, H. Hao, and L. Qin, "Experiment and model for the viscosity of carbonated N-methyldiethanolamine–diethanolamine aqueous solutions," *Journal of Molecular Liquids,* vol. 181, pp. 105-109, 2013.

[7]   R. Safdar, A. A. Omar, and B. Lal, "Performance of aqueous tetrabutylammonium hydroxide, piperazine and their blends for carbon dioxide capture," *Journal of Molecular Liquids,* vol. 266, pp. 522-528, 2018.

[8]   W. M. Budzianowski, *Energy Efficient Solvents for CO2 Capture by Gas-Liquid Absorption: Compounds, Blends and Advanced Solvent Systems*. Springer, 2016.

[9]   R. Ramazani, S. Mazinani, A. Hafizi, and A. Jahanmiri, "Equilibrium solubility of carbon dioxide in aqueous blend of monoethanolamine (MEA) and 2-1-piperazinyl-

ethylamine (PZEA) solutions: experimental and optimization study," *Process Safety and Environmental Protection,* vol. 98, pp. 325-332, 2015.

[10]   R. Ramazani, S. Mazinani, A. Hafizi, A. Jahanmiri, B. Van der Bruggen, and S. Darvishmanesh, "Solubility and absorption rate enhancement of CO2 in K2CO3," *Separation Science and Technology,* vol. 51, no. 2, pp. 327-338, 2016/01/22 2016.

[11]   J. Xie, F. Wang, and D. Fu, "Investigation of surface thermodynamics for DEAE-[N1111][Gly], DEAE-[Bmim][Gly] and DEAE-[Bmim][Lys] aqueous solutions," *Journal of Molecular Liquids,* vol. 249, pp. 1068-1074, 2018.

[12]   Z. Zhang, Y. Li, W. Zhang, J. Wang, M. R. Soltanian, and A. G. Olabi, "Effectiveness of amino acid salt solutions in capturing CO2: A review," *Renewable and Sustainable Energy Reviews,* vol. 98, pp. 179-188, 2018.

[13]   S. Garg, A. Shariff, M. Shaikh, B. Lal, H. Suleman, and N. Faiqa, "Experimental data, thermodynamic and neural network modeling of CO2 solubility in aqueous sodium salt of l-phenylalanine," *Journal of CO2 Utilization,* vol. 19, pp. 146-156, 2017.

[14]   Y. Zhao, S. Shen, Y. Bian, Y.-n. Yang, and U. Ghosh, "CO2 solubility in aqueous potassium lysinate solutions at absorber conditions," *The Journal of Chemical Thermodynamics,* vol. 111, pp. 100-105, 2017.

[15]   F. R. Abdeen, M. Mel, M. S. Jami, S. I. Ihsan, and A. F. Ismail, "A review of chemical absorption of carbon dioxide for biogas upgrading," *Chinese Journal of Chemical Engineering,* vol. 24, no. 6, pp. 693-702, 2016.

[16]   R. J. Hook, "An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds," *Industrial & engineering chemistry research,* vol. 36, no. 5, pp. 1779-1790, 1997.

[17]   A. Shojaeian and A. Haghtalab, "Solubility and density of carbon dioxide in different aqueous alkanolamine solutions blended with 1-butyl-3-methylimidazolium acetate ionic liquid at high pressure," *Journal of Molecular Liquids,* vol. 187, pp. 218-225, 2013.

[18]   H. Guo, H. Li, and S. Shen, "CO2 capture by water-lean amino acid salts: absorption performance and mechanism," *Energy & fuels,* vol. 32, no. 6, pp. 6943-6954, 2018.

[19]   M. E. Hamzehie and H. Najibi, "Carbon dioxide absorption in aqueous solution of potassium glycinate+ 2-amino-2-methyl-1-propanol as new absorbents," *RSC Advances,* vol. 6, no. 67, pp. 62612-62623, 2016.

[20]   S. Shen, Y.-n. Yang, Y. Wang, S. Ren, J. Han, and A. Chen, "CO2 absorption into aqueous potassium salts of lysine and proline: Density, viscosity and solubility of CO2," *Fluid Phase Equilibria,* vol. 399, pp. 40-49, 2015.

[21]   A. Aftab, A. Shariff, S. Garg, B. Lal, M. Shaikh, and N. Faiqa, "Solubility of CO2 in aqueous sodium β-alaninate: experimental study and modeling using Kent Eisenberg model," *Chemical Engineering Research and Design,* vol. 131, pp. 385-392, 2018.

[22]   H. M. Mohsin, A. M. Shariff, and K. Johari, "3-Dimethylaminopropylamine (DMAPA) mixed with glycine (GLY) as an absorbent for carbon dioxide capture and subsequent utilization," *Separation and Purification Technology,* vol. 222, pp. 297-308, 2019.

[23]   N. Aldenkamp, P. Huttenhuis, N. Penders-van Elk, E. Steinseth Hamborg, and G. F. Versteeg, "Solubility of carbon dioxide in aqueous potassium salts of glycine and taurine at absorber and desorber conditions," *Journal of Chemical & Engineering Data,* vol. 59, no. 11, pp. 3397-3406, 2014.

[24]   Z.-W. Chen, R. B. Leron, and M.-H. Li, "Equilibrium solubility of carbon dioxide in aqueous potassium L-asparaginate and potassium L-glutaminate solutions," *Fluid Phase Equilibria,* vol. 400, pp. 20-26, 2015.

[25]   W. M. Haynes, *CRC handbook of chemistry and physics*. CRC press, 2014.

[26]   A. F. Portugal, F. D. Magalhães, and A. Mendes, "Carbon dioxide absorption kinetics in potassium threonate," *Chem. Eng. Sci.,* vol. 63, p. 3493, 2008.

[27]   J. Lim, D. H. Kim, Y. Yoon, S. K. Jeong, K. T. Park, and S. C. Nam, "Absorption of CO2 into aqueous potassium salt solutions of L-alanine and L-proline," *Energy & Fuels,* vol. 26, p. 3910, 2012.

[28]   D. Guo *et al.*, "Amino Acids as Carbon Capture Solvents: Chemical Kinetics and Mechanism of the Glycine + CO2 Reaction," *Energy & Fuels,* vol. 27, no. 7, pp. 3898-3904, 2013/07/18 2013.

[29]   H. Thee, N. J. Nicholas, K. H. Smith, G. da Silva, S. E. Kentish, and G. W. Stevens, "A kinetic study of CO2 capture with potassium carbonate solutions promoted with various amino acids: Glycine, sarcosine and proline," *International Journal of Greenhouse Gas Control,* vol. 20, pp. 212-222, 2014/01/01/ 2014.

[30]   S.-W. Park, Y.-S. Son, D.-W. Park, and K.-J. Oh, "Absorption of Carbon Dioxide into Aqueous Solution of Sodium Glycinate," *Separation Science and Technology,* vol. 43, no. 11-12, pp. 3003-3019, 2008/08/08 2008.

[31]   S. Shen, Y.-n. Yang, Y. Bian, and Y. Zhao, "Kinetics of CO2 Absorption into Aqueous Basic Amino Acid Salt: Potassium Salt of Lysine Solution," *Environmental Science & Technology,* vol. 50, no. 4, pp. 2054-2063, 2016/02/16 2016.

[32]   S. Shen, Y. Zhao, Y. Bian, Y. Wang, H. Guo, and H. Li, "CO2 absorption using aqueous potassium lysinate solutions: vapor–liquid equilibrium data and modelling," *The Journal of Chemical Thermodynamics,* vol. 115, pp. 209-220, 2017.

[33]   Y. Zhao *et al.*, "A comparative study of aqueous potassium lysinate and aqueous monoethanolamine for postcombustion CO2 capture," *Energy & fuels,* vol. 31, no. 12, pp. 14033-14044, 2017.

[34]   D. M. Muñoz, A. F. Portugal, A. E. Lozano, G. José, and J. de Abajo, "New liquid absorbents for the removal of CO 2 from gas mixtures," *Energy & Environmental Science,* vol. 2, no. 8, pp. 883-891, 2009.

[35]   P. Pakzad, M. Mofarahi, A. A. Izadpanah, M. Afkhamipour, and C.-H. Lee, "An experimental and modeling study of CO2 solubility in a 2-amino-2-methyl-1-propanol (AMP)+ N-methyl-2-pyrrolidone (NMP) solution," *Chemical Engineering Science,* vol. 175, pp. 365-376, 2018.

[36]   J.-I. Baek and J.-H. Yoon, "Solubility of carbon dioxide in aqueous solutions of 2-amino-2-methyl-1, 3-propanediol," *Journal of Chemical & Engineering Data,* vol. 43, no. 4, pp. 635-637, 1998.

[37]   F.-Y. Jou, F. D. Otto, and A. E. Mather, "Vapor-liquid equilibrium of carbon dioxide in aqueous mixtures of monoethanolamine and methyldiethanolamine," *Industrial & engineering chemistry research,* vol. 33, no. 8, pp. 2002-2005, 1994.

[38]   R. Hamidi, M. Farsi, and R. Eslamloueyan, "CO2 solubility in aqueous mixture of MEA, MDEA and DAMP: Absorption capacity, rate and regeneration," *Journal of Molecular Liquids,* vol. 265, pp. 711-716, 2018/09/01/ 2018.

[39]   C. Perinu, I. M. Bernhardsen, H. F. Svendsen, and K.-J. Jens, "CO2 Capture by Aqueous 3-(Methylamino)propylamine in Blend with Tertiary Amines: An NMR Analysis," *Energy Procedia,* vol. 114, pp. 1949-1955, 2017/07/01/ 2017.

[40]   Y. Matsuzaki, H. Yamada, F. A. Chowdhury, T. Higashii, S. Kazama, and M. Onoda, "Ab Initio Study of CO2 Capture Mechanisms in Monoethanolamine Aqueous Solution: Reaction Pathways from Carbamate to Bicarbonate," *Energy Procedia,* vol. 37, pp. 400-406, 2013/01/01/ 2013.

[41] D. Fu, P. Zhang, and L. Wang, "Absorption performance of CO2 in high concentrated [Bmim][Lys]-MDEA aqueous solution," *Energy,* vol. 113, pp. 1-8, 2016.

[42] D. Koschel, J.-Y. Coxam, L. Rodier, and V. Majer, "Enthalpy and solubility data of CO2 in water and NaCl (aq) at conditions of interest for geological sequestration," *Fluid phase equilibria,* vol. 247, no. 1-2, pp. 107-120, 2006.

Graphical abstract
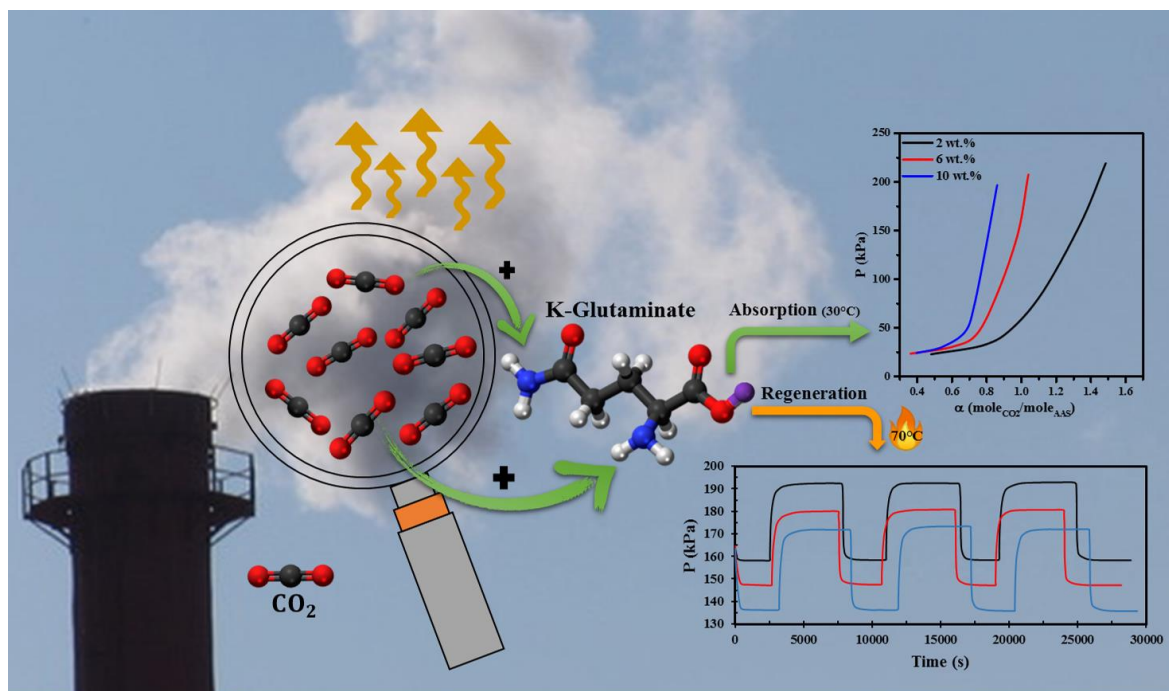
Research Highlight:

- CO_2 solubility and absorption rate measured in K-Glu solution at different conditions

- Achievement of higher performance and rate as compared to conventional amines

- Heat of absorption and kinetic revealed high activity and economic regeneration of K-Glu