

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231538669>

Solubility (at Low Partial Pressures), Density, Viscosity, and Corrosion Rate of Carbon Dioxide in Blend Solutions of Monoethanolamine (MEA) and Sodium Glycinate (SG)

ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · JUNE 2011

Impact Factor: 2.04 · DOI: 10.1021/jc2002418

CITATIONS

20

READS

49

3 AUTHORS, INCLUDING:



Saeed Mazinani

University of Leuven

19 PUBLICATIONS 64 CITATIONS

SEE PROFILE

Solubility (at Low Partial Pressures), Density, Viscosity, and Corrosion Rate of Carbon Dioxide in Blend Solutions of Monoethanolamine (MEA) and Sodium Glycinate (SG)

Saeed Mazinani, Aria Samsami, and Abdolhossein Jahanmiri*

Department of Chemical Engineering, Chemical and Petroleum Engineering School, Shiraz University, Shiraz 71345, Iran

Alireza Sardarian

Department of Chemistry, Faculty of Science, Shiraz University, Shiraz, Iran

ABSTRACT: The influence of the sodium glycinate (SG) on the solubility of carbon dioxide (CO₂) in monoethanolamine (MEA) was investigated. The equilibrium solubilities of CO₂ into blend solutions of SG and MEA were measured experimentally with a stirred batch reactor for the molar ratio of SG between 0.2 and 0.8 in total blend concentration (C_T) 2.5 mol·dm⁻³ (M) over the temperature and CO₂ partial pressure ranging from (298 to 313) K and (0 to 35) kPa, respectively. The results of the CO₂ solubility are expressed as CO₂ loading (mol CO₂/mol blend solution) as a function of partial pressure of CO₂ for all experimental runs. The densities and viscosities of the blend solutions were measured at the same conditions of the solubility measurement. Some corrosion rate tests were also performed on carbon steel at a temperature of 308 K. Experimental results showed that, with increasing the molar ratio of SG in total blend concentration, the viscosity and corrosion rate of blend solutions increase.

INTRODUCTION

The removal of CO₂ from gas streams for a number of technical and economical reasons is an important operation in many industrial processes. The presence of CO₂ in natural gas reduces the heating value and as an acidic gas can cause corrosion in process equipment. In liquefied natural gas (LNG) plants (natural gas that has been converted temporarily to liquid form for ease of storage or transport), CO₂ will freeze if not removed in the low-temperature chillers and also poisons the catalysts in the ammonia synthesis process.¹ According to the Intergovernmental Panel on Climate Change (IPCC), increasing emissions of greenhouse gases (GHG) will rise the average global temperature by (1.1 to 6.4) °C by the end of the 21st century.² Climate models established by the IPCC show that dramatic climate effects will take place if the average of global temperature increases by more than 2 °C. To avoid such a high temperature increase, global GHG emissions should be reduced by (50 to 80) % by 2050.³ CO₂ is the largest component of GHG being emitted to the atmosphere and currently responsible for over 60 % of the enhanced greenhouse effect, so it is regarded as most important greenhouse gas.⁴ Hence, the reduction of CO₂ emissions should be considered urgently to slow down the trend of Earth's surface temperature. There are several technologies available for removing CO₂ from gas streams. These include chemical and physical absorption, cryogenic separation, physical adsorption, membrane separation, and biological fixation.^{5,6} Among these techniques, chemical absorption by alkanolamines is an effective and reliable method for capturing CO₂ from process gas. Aqueous MEA solution is the most common solvent proposed for CO₂ capture which has been widely used as an industrial absorbent because of high absorption rate, low solvent cost, high resistance to thermal degradation, low molecular weight, and low solubility

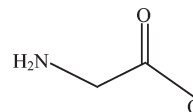


Figure 1. Molecular structure of glycine.

for hydrocarbons.⁷ However, it has some disadvantages including low CO₂ loading, high energy requirements for regeneration, degradation through oxidation of the amine, vaporization losses because of high vapor pressure, and high viscosity, and also it can cause operational problems such as corrosion, foaming, and fouling of the process equipment.^{8–10}

Recently, for eliminating these problems the use of mixtures of chemical solvents in varying concentrations has been receiving a great deal of interest because it combines the favorable features of different chemical absorbents while suppressing the unfavorable, therefore producing absorbents with excellent characteristics.

Because the equilibrium solubility data have a very important role in the design and optimization of industrial gas absorption units, many researchers have been interested in this field. For example, Li and Chang¹¹ presented the equilibrium solubility of CO₂ in aqueous of MEA with 2-amino-2-methyl-1-propanol (AMP) at partial pressures ranging from (0.1 to 200) kPa and temperatures between (40 and 100) °C. Li and Lee¹² measured the solubility and diffusivity of CO₂ and N₂O in diethanolamine (DEA) with *N*-methyldiethanolamine (MDEA) and with AMP in the temperature range of (30 to 40) °C. Kundu and

Received: March 9, 2011

Accepted: June 6, 2011

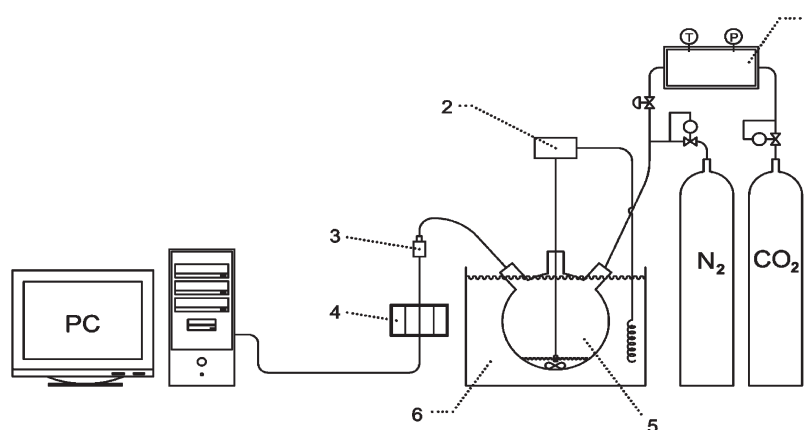


Figure 2. Schematic diagram of the experimental setup: 1, syringe gas; 2, temperature indicator; 3, pressure indicator; 4, data logger; 5, equilibrium cell; 6, water bath.

Table 1. Experimental Conditions Used in This Work

partial pressure of CO ₂ (kPa)	0 to 35
temperature of the liquid (<i>T</i>)/K	298 to 313
mole ratio of SG in total blend concentration	0.2 to 0.8
total blend concentration (<i>C_T</i>)/mol·dm ⁻³	2.5
pH of the deionized water	6.95

Bandyopadhyay¹³ presented new experimental results for the CO₂ solubility in aqueous blends of DEA with AMP in the temperature range of (303 to 323) K and CO₂ partial pressure from (1 to 100) kPa. Mondal¹⁴ determined the solubility of CO₂ in aqueous blends of DEA and piperazine (PZ) for temperatures and CO₂ partial pressures ranging from (303.14 to 353.14) K and (10.133 to 20.265) kPa, respectively. Cheng et al.¹⁵ experimentally examined the solubility of CO₂ in the aqueous blends of MEA and triethanolamine (TEA) at temperatures of (313.2, 333.2, 353.2, and 373.2) K and CO₂ partial pressure from (0.1 to 120) kPa.

Amino-acid salts provide several interesting properties such as high absorbing capacity, favorable binding energy, good stability to oxidative degradation, and low vapor pressures and viscosities.^{16,17} Song et al.¹⁸ measured the solubilities of CO₂ in aqueous (0.10, 0.20, and 0.30) mass fraction sodium glycinate (SG) solutions at (303.15, 313.15, and 323.15) K over the partial pressure of carbon dioxide ranging from (0.1 to 200) kPa in an equilibrium cell. Portugal et al.¹⁹ measured the solubility of CO₂ in aqueous solution of potassium glycinate (PG) at temperatures from (293 to 351) K for concentrations ranging between (0.1 and 3) M and CO₂ partial pressures up to 0.6 bar. They concluded that amino acid salt solutions can be very interesting for CO₂ absorption since they have high absorption capacities. Because of these advantages, amino acid salts are an option for the combination with industrial gas-treating solvents such as MEA.

In this work, the effect of SG addition on the solubility of CO₂ in MEA solutions has been investigated. (Glycine is the simplest member of the amino acid family. The molecular structure of glycine has been shown in Figure 1.) New experimental data on equilibrium solubility of CO₂ in aqueous blend solutions of MEA and SG have been obtained at temperatures of (298, 308, and 313) K over the CO₂ partial pressure range (0 to 35) kPa for molar ratio of SG from 0.2 to 0.8 in a total blend concentration of 2.5 M. Also, the experimental values of the densities, viscosities, and corrosion rates of the solutions are presented.

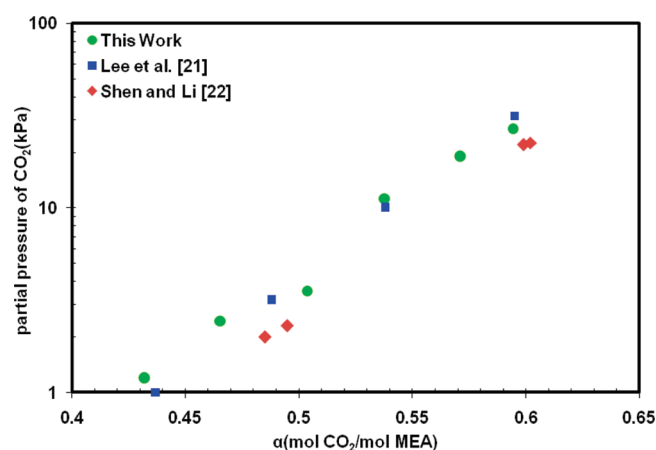


Figure 3. Solubility of CO₂ in aqueous 2.5 M MEA solution at 313 K.

EXPERIMENTAL SECTION

Materials. Glycine (purity > 99.5 %), MEA (purity > 99.5 %), and sodium hydroxide (NaOH) (purity > 99 %) were obtained from Merck Chemical Company. CO₂ with a purity of > 99.9 % was supplied from commercial cylinders. The aqueous solutions of the amino acid salts were prepared by adding to the amino acid an equimolar amount of NaOH in a volumetric flask filled with deionized water.

Solubility. The apparatus used to measure the solubility of CO₂ is a modification of the one applied by Derks et al.¹ The schematic diagram of the experimental setup has been shown in Figure 2, and conditions used in this work are presented in Table 1. The batch reactor (round-bottomed flask) with an internal volume (~2000 mL) was made of Pyrex. Both the reactor and the syringe gas were equipped with a temperature and pressure indicator.

In a typical experiment, when the apparatus was brought to the desired temperature, a known volume of fresh solution was transferred into the reactor vessel, and nitrogen gas was purged into cell to remove remaining air. Then, the syringe gas was filled with pure CO₂, and the initial pressure in the syringe was measured. When the vapor–liquid equilibrium is established, a certain amount of CO₂ was transferred into the reactor. The solution was continuously stirred with the magnetic stirrer to

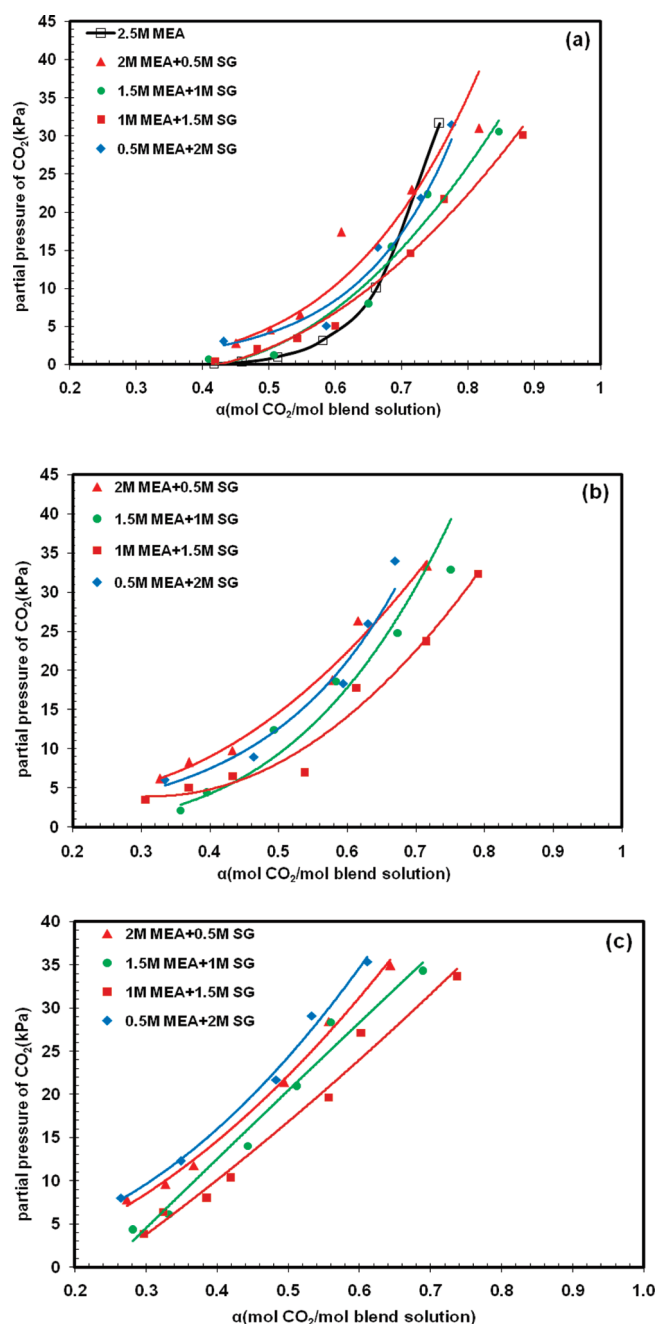


Figure 4. Solubility of carbon dioxide into blends of MEA and SG solutions in different molar ratios of SG in total blend concentration (C_T) = 2.5 M at (a) 298 K, (b) 308 K, and (c) 313 K.

increase the mass transfer rate and achieve equilibrium quickly. The contents of the reactor were allowed to reach equilibrium at the desired temperature. As the carbon dioxide is absorbed, the total pressure decreases. During the experiment, the pressure of system was measured with time by a gauge pressure transmitter sensor (GEFRAN) with an accuracy of ± 0.1 kPa, and the temperature was controlled by means of a thermostatic water bath with a precision of ± 0.1 °C. The measured data were sent to computer via a data logger and recorded by Lab View software. When the total pressure of the cell remained steady-state for 2 h, the equilibrium was assumed to be reached. The partial pressure of CO₂ was calculated from the difference between initial and

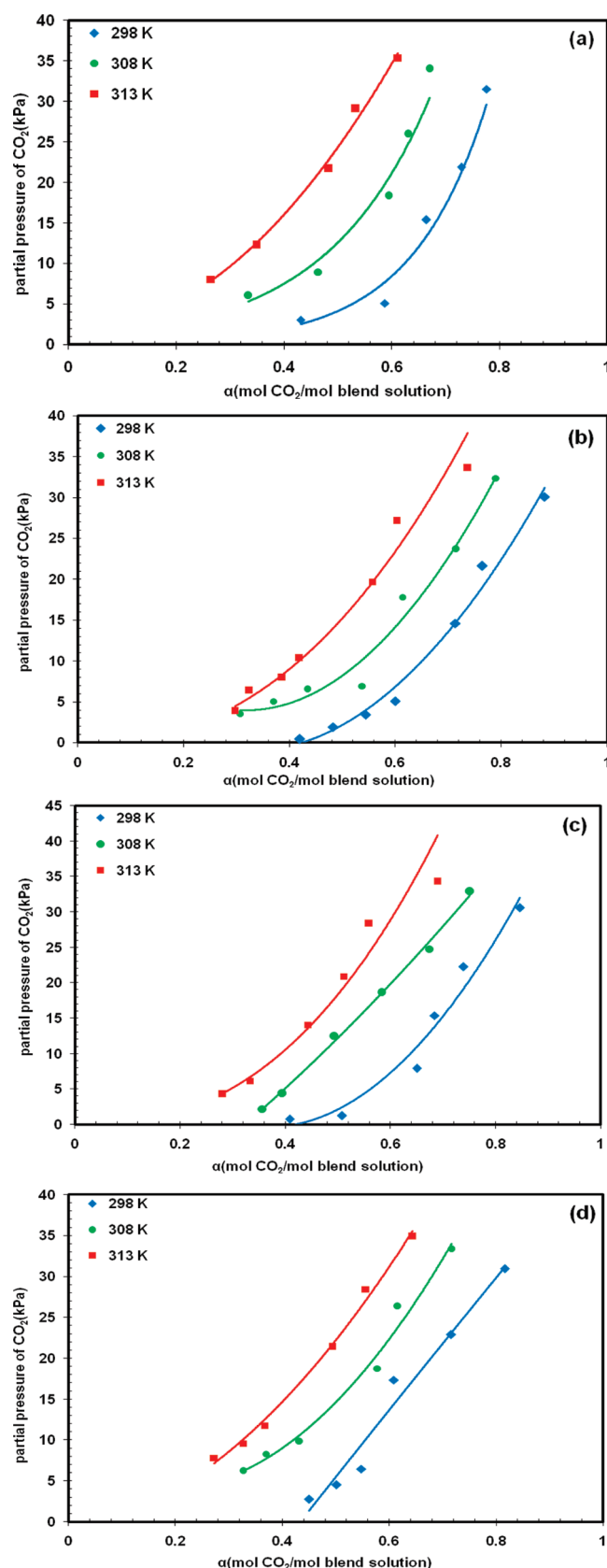


Figure 5. Solubility of CO₂ into blends of MEA and SG solutions in different temperatures at (a) 2 M MEA + 0.5 M SG, (b) 1.5 M MEA + 1 M SG, (c) 1 M MEA + 1.5 M SG, and (d) 0.5 M MEA + 2 M SG.

Table 2. Solubilities (α = mol CO₂/mol Blend Solution) of CO₂ in MEA + SG Solutions

2 M MEA + 0.5 M SG		1.5 M MEA + 1 M SG		1 M MEA + 1.5 M SG		0.5 M MEA + 2 M SG	
P_{CO_2} (kPa)	α	P_{CO_2} (kPa)	α	P_{CO_2} (kPa)	α	P_{CO_2} (kPa)	α
$T = 298 \text{ K}$							
2.7	0.451	0.7	0.409	0.4	0.419	3.0	0.431
4.5	0.502	1.2	0.508	1.9	0.482	5.1	0.587
6.5	0.547	7.9	0.651	3.4	0.544	15.4	0.664
17.3	0.609	15.4	0.684	5.1	0.601	21.9	0.729
22.9	0.716	22.3	0.739	14.6	0.713	31.5	0.776
31	0.816	30.6	0.847	21.6	0.764		
				30.1	0.882		
$T = 308 \text{ K}$							
6.2	0.327	2.2	0.357	3.5	0.307	6.0	0.334
8.3	0.369	4.4	0.395	5.0	0.370	8.9	0.464
9.8	0.432	12.4	0.494	6.5	0.434	18.3	0.594
18.8	0.579	18.6	0.583	6.9	0.538	26.0	0.630
26.4	0.616	24.8	0.674	17.8	0.614	34.0	0.671
33.3	0.716	32.9	0.751	23.7	0.715		
				32.3	0.790		
$T = 313 \text{ K}$							
7.8	0.273	4.3	0.281	3.8	0.297	8.0	0.265
9.6	0.327	6.1	0.333	6.4	0.324	12.3	0.349
11.8	0.367	14	0.443	8.0	0.386	21.7	0.483
21.4	0.494	20.9	0.512	10.3	0.419	29.1	0.533
28.4	0.557	28.3	0.560	19.7	0.557	35.3	0.612
34.9	0.644	34.3	0.689	27.1	0.603		
				33.6	0.737		

Table 3. Densities ($\rho/\text{g}\cdot\text{cm}^{-3}$; part a) and Viscosities ($\mu/\text{mPa}\cdot\text{s}$; part b) of MEA + SG Solutions

(a) $\rho/\text{g}\cdot\text{cm}^{-3}$				
T (K)	2 M MEA + 0.5 M SG	1.5 M MEA + 1 M SG	1 M MEA + 1.5 M SG	0.5 M MEA + 2 M SG
298	1.0292	1.0519	1.0752	1.0987
308	1.0267	1.0493	1.0724	1.0967
313	1.0244	1.0474	1.0702	1.0945
(b) $\mu/\text{mPa}\cdot\text{s}$				
T (K)	2 M MEA + 0.5 M SG	1.5 M MEA + 1 M SG	1 M MEA + 1.5 M SG	0.5 M MEA + 2 M SG
298	1.461	1.620	1.768	1.962
308	1.218	1.323	1.447	1.553
313	1.087	1.194	1.303	1.385

final (equilibrium) vessel pressure corrected for the vapor pressure of the fresh solution. The CO₂ loading of solution at a certain CO₂ partial pressure was calculated by ideal gas law. In different tests, several known volumes of pure CO₂ were transferred into the reactor.

Density and Viscosity. The densities of blend solutions were measured by using of calibrated pycnometers. To determine volumes of pycnometers at various temperatures from (298 to 313) K, triple-distilled water was used as a standard substance. The tests were carried out in a temperature water bath with a precision of 0.01 °C. An analytical balance (A&D, D0001) with

accuracy of 0.0001 g was used for weighing the amounts of solution. The uncertainty of measurement was 0.0001 g·cm⁻³.

To determine the kinematic viscosities of the mixtures solutions, several Ubbelohde viscometers with various capillary sizes were used. An appropriate viscometer was selected in consideration of the estimated values of kinematic viscosity. Kinematic viscosities were calculated from the efflux times measured by means of a chronometer with an accuracy of 0.01 s in a water bath with the precision of 0.01 °C (JULABO, ME). The kinematic viscosity values were reproducible within $\pm 1\%$. The dynamic

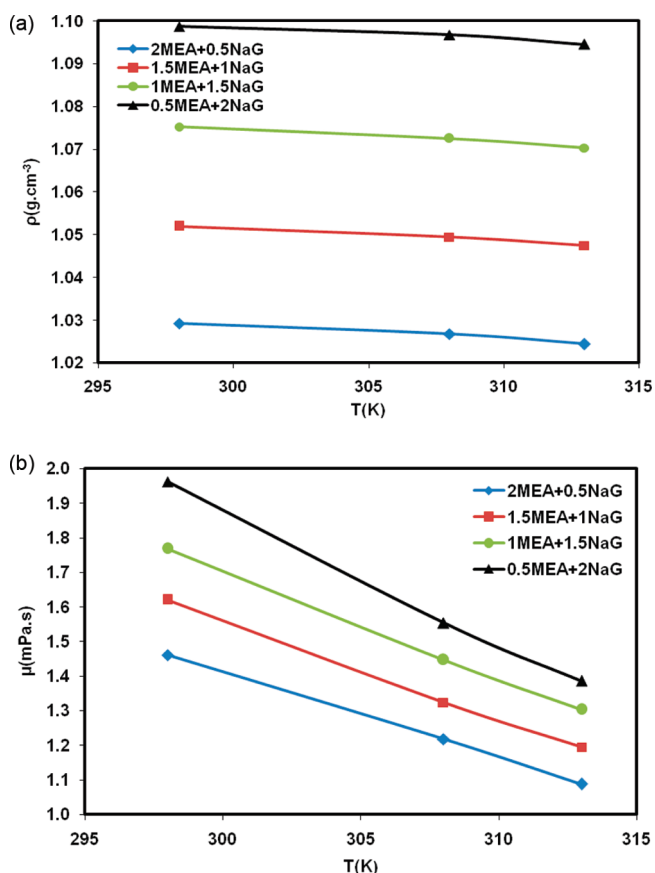


Figure 6. Densities ($\rho/\text{g}\cdot\text{cm}^{-3}$; part a) and viscosities ($\mu/\text{mPa}\cdot\text{s}$; part b) of MEA + SG solutions.

Table 4. Corrosion Rates (mmpy = Millimeter per Year) of MEA + SG Solutions at 308 K

corrosion rate (mmpy)	
2 M MEA + 0.5 M SG	$1.0\cdot 10^{-3}$
1.5 M MEA + 1 M SG	$1.3\cdot 10^{-3}$
1 M MEA + 1.5 M SG	$1.6\cdot 10^{-3}$
0.5 M MEA + 2 M SG	$2.4\cdot 10^{-3}$

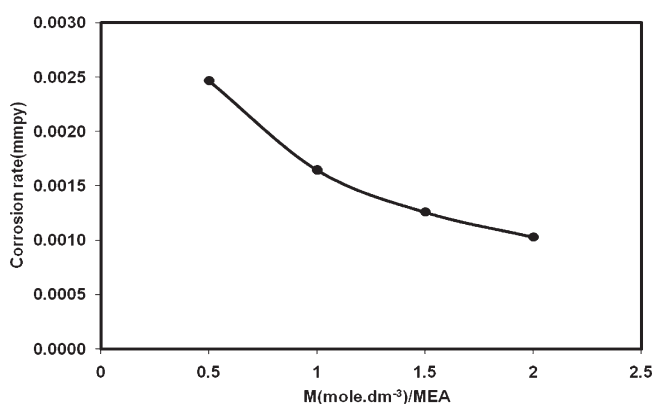


Figure 7. Corrosion rates (mmpy = millimeter per year) of MEA + SG solutions at 308 K.

viscosities were calculated by multiplying the kinematic viscosities with the measured density values of the same solutions.

Corrosion Rate. The electrochemical technique was used to study the corrosion rates of aqueous blends of MEA and SG. Corrosion rate experiments were conducted using a potentiostat unit (AUTO LAB, 302N) at a corrosion temperature of 308 K. The reference electrode is Ag/AgCl (3 M KCl), and the counter electrode is a rod of Pt. The tested specimens were carbon steel with spherical shape having a surface area of 1.13 cm^2 ($6\text{ mm} \times 6\text{ mm}$). Before the tests, the specimens were wet ground with silicon carbide paper (grade 400) and water, then wet polished with silicon carbide paper (grade 600) to obtain a homogeneous surface, rinsed with deionized water and finally with acetone, then dried with air, and kept in a desiccator. After the tests, the specimens were washed and dried again. The entire corrosion rate tests were performed in accordance with ASTM G5-94.²⁰

RESULTS AND DISCUSSION

The experimental setup and procedure were tested by measuring the solubility of CO_2 in aqueous 2.5 M MEA solution at 313 K and compared with the previously reported data in literature as shown in Figure 3.^{21,22}

For studying the effect of SG on the CO_2 loading of MEA, the equilibrium solubility of CO_2 in aqueous blends of MEA and SG was measured for molar ratios of SG between 0.2 and 0.8 in total blend concentration at temperatures of (298, 308, and 313) K as shown graphically in Figure 4a–c and listed in Table 2. The maximum CO_2 loading occurred at a 0.6 (1 M MEA + 1.5 M SG) molar ratio of SG in total blend concentration. It can be seen that, at CO_2 partial pressures higher than 20 kPa, aqueous solutions of MEA + SG have better CO_2 loading than pure MEA solution in the order 1 M MEA + 1.5 M SG > 1.5 M MEA + 1 M SG > 2 M MEA + 0.5 M SG > 0.5 M MEA + 2 M SG > MEA. At optimum molar ratio (0.6), the binary interaction between MEA and SG has its minimum value. On the other hand, far from the optimum molar ratio, the hydrogen bond of solution is stronger which leads to the reduction of CO_2 loading.

Figure 5a–d shows the effect of temperature on the solubility of CO_2 into aqueous blends of MEA and SG where temperature was varied from (298 to 313) K. It is clear that, while temperature increases, the CO_2 loading of blend solutions decreases at a particular total concentration. The absorption of CO_2 by chemical solvents is an exothermic reaction in nature, thus in accordance with Le Chatelier's principle that an increase in temperature results in decreasing the extent of CO_2 absorption.

The experimental values of densities and viscosities of aqueous blends of MEA + SG solutions at temperatures of (298, 308, and 313) K are presented in Table 3 and illustrated in Figure 6. The results show that, with the increasing molar ratio of SG in total blend concentration, the viscosities of blend solutions increase because SG is an ionic compound; it can enhance the ionic strength of the solution which results in increased viscosity of the solution.

The experimental results of corrosion rate tests which were performed at 308 K are tabulated in Table 4 and plotted in Figure 7. In these tests, the corrosion rates of solutions mixtures were studied on carbon steel coupons in the absence of dissolved CO_2 . The results indicate that corrosion rates of blend solutions increase with increasing molar ratio of SG in total blend concentration; since SG behaves as a base, it produces OH in

the solution causing it to increase the PH, and as a result the corrosion will be accelerated.

CONCLUSION

In this work, SG as a potential CO₂ absorbent (high CO₂ loading) was blended with MEA (high reaction rate with CO₂). The solubility of CO₂ into solutions of MEA + SG was measured over a CO₂ partial pressure range of (0 to 35) kPa and a temperature range of (298 to 313) K. The densities and viscosities of solutions were determined at temperatures between (298 and 313) K. The corrosion rates of solutions were also measured at a temperature of 308 K. Experimental results showed that the influence of SG on the solubility of CO₂ in MEA solutions is considerable. However, it has a negative effect on the viscosity and corrosion rate of solutions. It is interesting to note here that, at CO₂ partial pressures higher than 20 kPa, the CO₂ loading of MEA + SG aqueous solutions were higher than that of aqueous MEA solution. The mixed solvent MEA + SG demonstrate a potential in the absorption of CO₂ at relatively low partial pressures. The actual possibility of these mixed solvents absorbing CO₂ will be justified with the kinetic data measured later.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +98 61 33788; fax: +98 62 85118. E-mail: jahanmir@shirazu.ac.ir.

REFERENCES

- (1) Derks, P. W. J.; Dijkstra, H. B. S.; Hogendoorn, J. A.; Versteeg, G. F. Solubility of carbon dioxide in aqueous piperazine solutions. *AIChE J.* **2005**, *51*, 2311–2327.
- (2) The Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007: The Physical Science Basis*; Cambridge University Press: Cambridge, U.K., 2007.
- (3) The Intergovernmental Panel on Climate Change (IPCC). *IPCC Third Assessment Report-Climate Change 2001*; Cambridge University Press: Cambridge, U.K., 2001.
- (4) Williams, M. *Climate change: information kit*; United Nations Environment Programme (UNEP) and the United Nations Framework Convention on Climate Change (UNFCCC): Geneva, 2002.
- (5) Kimura, N.; Omata, K.; Kiga, T.; Takano, S.; Shikisma, S. Characteristics of pulverized coal combustion in O₂/CO₂ mixtures for CO₂ recovery. *Energ. Convers. Manage.* **1995**, *36*, 805–808.
- (6) Wolsky, A. M.; Daniels, E. J.; Jody, B. J. CO₂ capture from the flue gas of conventional fossil-fuel-fired power plants. *Environ. Prog.* **1994**, *13*, 214–219.
- (7) Ma'mun, S.; Svendsen, H.; Hoff, A.; Juliussen, O. Selection of new absorbents for carbon dioxide capture. *Energ. Convers. Manage.* **2007**, *48*, 251–258.
- (8) Jou, F. Y.; Mather, A. E.; Otto, F. D. The solubility of CO₂ in a 30 mass percent monoethanolamine solution. *Can. J. Chem. Eng.* **1995**, *73*, 140–147.
- (9) Liu, Y.; Zhang, L.; Watanasiri, S. Representing vapor-liquid equilibrium for an aqueous MEA-CO₂ system using the electrolyte nonrandom-two-liquid model. *Ind. Eng. Chem. Res.* **1999**, *38*, 2080–2090.
- (10) Li, Y. G.; Mather, A. E. Correlation and prediction of the solubility of carbon dioxide in a mixed alkanolamine solution. *Ind. Eng. Chem. Res.* **1994**, *33*, 2006–2015.
- (11) Li, M. H.; Chang, B. C. Solubilities of carbon dioxide in water + monoethanolamine + 2-amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **1994**, *39*, 448–452.
- (12) Li, M. H.; Lee, W. C. Solubility and diffusivity of N₂O and CO₂ in diethanolamine + N-methyldiethanolamine + water and in diethanolamine

+ 2-amino-2-methyl-1-propanol + water. *J. Chem. Eng. Data* **1996**, *41*, 551–556.

(13) Kundu, M.; Bandyopadhyay, S. S. Solubility of CO₂ in water + diethanolamine + 2-amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **2006**, *51*, 398–405.

(14) Mondal, M. K. Solubility of carbon dioxide in an aqueous blend of diethanolamine and piperazine. *J. Chem. Eng. Data* **2009**, *54*, 2381–2385.

(15) Cheng, M. D.; Caparanga, A. R.; Soriano, A. N.; Li, M. H. Solubility of CO₂ in the solvent system water + monoethanolamine + triethanolamine. *J. Chem. Eng. Data* **2010**, *42*, 342–347.

(16) Kumar, P.; Hogendoorn, J.; Feron, P. H. M.; Versteeg, G. F. Density, viscosity, solubility, and diffusivity of N₂O in Aqueous Amino Acid Salt Solutions. *J. Chem. Eng. Data* **2001**, *46*, 1357–1361.

(17) Kumar, P.; Hogendoorn, J.; Feron, P. H. M.; Versteeg, G. F. Equilibrium solubility of CO₂ in aqueous potassium taurate solutions: Part I. Crystallization in carbon dioxide loaded aqueous salt solutions of amino acids. *Ind. Eng. Chem. Res.* **2003**, *42*, 2832–2840.

(18) Song, H. J.; Lee, S.; Maken, S.; Park, J. J.; Park, J. W. Solubilities of carbon dioxide in aqueous solutions of sodium glycinate. *Fluid Phase Equilib.* **2006**, *246*, 1–5.

(19) Portugal, A. F.; Sousa, J. M.; Magalhães, F. D.; Mendes, A. Solubility of carbon dioxide in aqueous solutions of amino acid salts. *Chem. Eng. Sci.* **2009**, *64*, 1993–2002.

(20) Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements. In *Annual Book of ASTM Standards*; American Society of Testing and Materials: West Conshohocken, PA, 2004.

(21) Lee, J. I.; Otto, F. D.; Mather, A. E. Equilibrium between carbon dioxide and aqueous monoethanolamine solutions. *J. Appl. Chem. Biotechnol.* **1986**, *26*, 541–549.

(22) Shen, K. P.; Li, M. H. Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyldiethanolamine. *J. Chem. Eng. Data* **1992**, *37*, 96–100.