Solubilities of Carbon Dioxide and Densities of Aqueous Sodium Glycinate Solutions before and after CO_2 Absorption

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The densities of aqueous solutions of sodium glycinate (SG) were measured for a range of concentrations [(1, 5, 10, 15, 20, and 30) % wt] and at a temperature range (298.15 to 353.15) K. The solubility of CO_2 in aqueous solution of sodium glycinate was measured for the same concentration range and at two temperatures (298.15 and 313.15) K, over CO_2 partial pressure ranging from (100 to 2500) kPa. The densities of aqueous solutions of sodium glycinate after the absorption were also measured at the same conditions of the solubility measurements. It was found that density of aqueous solutions of sodium glycinate increases as the molar concentration increases and decreases with an increase in temperature. The solubilities of CO_2 are reported as loading capacity (mol CO_2/mol SG) as a function of partial pressure of CO_2 at the corresponding temperature. It was found that CO_2 solubility increases with increase in CO_2 partial pressure. It was also found that solubility of sodium glycinate solution decreases with increasing sodium glycinate concentration and temperature. The densities of aqueous sodium glycinate after absorption gave a higher value than that before absorption and increase with increasing pressure.

Introduction

Natural gas is a fossil fuel that contains hydrocarbon (such as methane, ethane, propane, butane, and few heavier components), water, and impurities like CO_2, SO_2, and mercaptan (R-SH).[1] Acid gases like carbon dioxide (CO_2) and sulfur dioxide (SO_2) need to be removed from natural gas to increase the purity, heating value, and commercial value of natural gas. Failing to remove the two components will not allow the natural gas to be processed to form pipe line gas (carbon dioxide less than 4 %) or liquefied natural gas (carbon dioxide content less than 20 ppm).[2] Acid gases can also lead to corrosion of pipes and the other processing equipment. The removal of acid gas such as CO_2 and H_2S by absorption using reactive solvent has been the most commonly used method in industries. For this purpose, aqueous alkanolamine solutions have been used currently as reactive solvent due to its high reactivity, low cost, and high thermal stability. But alkanolamines especially monoethanalamine (MEA) have problems like degradation through oxidation of the amine, loss of amine during the stripping process, and foaming.[3] Very recently, it has been observed by the researchers that alkanolamines could be replaced with amino acid salts as an alternative solvent for CO_2 absorption because of its molecular similarity.[4−7] Though amino acids are more expensive than alkanolamines, they have certain unique advantages due to their physical and chemical properties.[4,5]

One of the amino acid salts which has the potential for the capture of CO_2 is sodium glycinate (SG). Physical properties of aqueous sodium glycinate as an absorbent for carbon dioxide removal have been studied previously.[8] Solubility of carbon dioxide in aqueous solutions of sodium glycinate at low pressure has also been studied experimentally.[9] Hence, in the present work, the density of aqueous solutions of sodium glycinate (SG) were measured for a range of concentrations, [(1, 5, 10, 15, 20, 30) % wt], and at a temperature range (298.15 to 353.15) K. The solubility of CO_2 in an aqueous solution of sodium glycinate was measured for the same range of concentrations and at temperatures (298.15 and 313.15) K, for CO_2 partial pressure ranging from (1 to 25) bar. The densities of aqueous solutions of sodium glycinate after the absorption were also measured at the same conditions of the solubility measurement. During the design and scale up of any absorber, the physical properties of the pure solvents were considered normally. But in some cases, if the changes in the physical properties of the solvents are substantial after absorption, it will lead to the malfunctioning of the absorber unit or reduction in absorption efficiency. Hence, in the present work, the densities of aqueous sodium glycinate solutions before and after CO_2 absorption were made and compared.

Experimental Section

Materials. The chemical absorbent used in this study is sodium glycinate ($C_2H_4NO_2Na$). Aqueous sodium glycinate was prepared by neutralizing glycine (purity ≥ 99.7 %, Merck), dissolved in distilled water, with equimolar sodium hydroxide (purity ≥ 99 %, R&M Chemicals). The concentration of the amino acid salt was estimated by titrating with standard HCl solutions. The end point is the isoelectric point of glycine. The concentration of sodium glycinate solution was found to be accurate within 1.0 %. Solution concentration ranging from (1 to 30) % wt was used in the present study. All weight measurements were done using an analytical balance with an accuracy of ± 0.1 mg. High purities of carbon dioxide and nitrogen (min. 99.8 %) were used for the experiments. Analytical grade barium chloride (purity > 99 % p.a., Fluka), hydrochloric acid (36 % p.a., SYSTERM), and sodium carbonate (purity > 99.5 %, SYSTERM) were used for the determination of the CO_2 absorbed in the aqueous sodium glycinate solutions.

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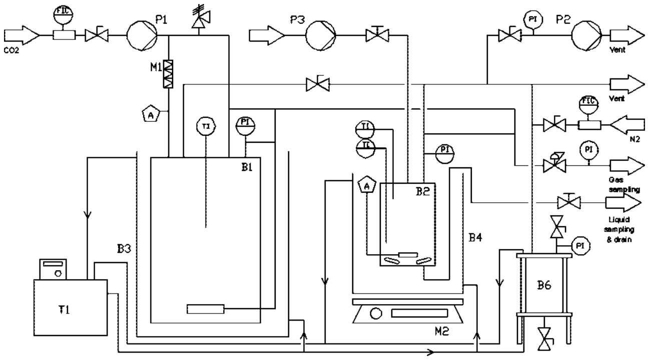

Figure 1. Schematic diagram of SOLTEQ BP-22 high pressure solubility cell. B1, mixing vessel; B2, equilibrium cell; B3, heating jacket for B1; B4, heating jacket for B2; B6, liquid degassing unit; M1, static mixer; M2: magnetic stirrer; T1, thermostat heating bath; P1, gas booster; P2, vacuum pump; P3, liquid pump.

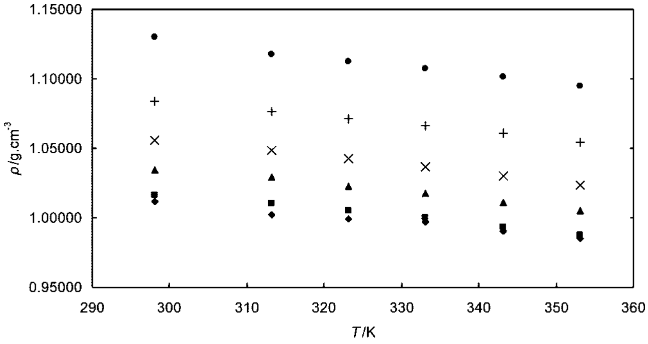

Figure 2. Density as a function of temperature for aqueous sodium glycinate solutions of different concentrations: ◆, 1 % wt; ■, 5 % wt; ▲, 10 % wt; ×, 15 % wt; +, 20 % wt; ●, 30 % wt.

Apparatus and Procedure

A. Density Measurement. The densities (ρ) of aqueous sodium glycinate solutions before and after the absorption were measured by an Anton Paar DMA-5000 digital vibrating-tube density meter. The equipment was calibrated by Millipore Ultrapure Water standard and ambient air. The precision of the experimental measurements have been found to be better than ± 0.00002 $g\cdot cm^{-3}$.[10]

B. Solubility Measurement. Solubility tests for the present study were done using a SOLTEQ BP-22 high pressure solubility cell. Initially, the mixing vessel was pressurized with CO_2 and heated to the desired pressure and temperature. Approximately 5 mL of aqueous sodium glycinate solution was fed into the equilibrium cell of 50 mL capacity, which was previously purged with nitrogen and vacuumed up to −0.95 atm. The apparatus was then brought to a desired temperature, and CO_2 was introduced from the mixing vessel to achieve total system pressure in the range of (100 to 2500) kPa. The solution was continuously stirred with a magnetic stirrer to enhance the solubility in the system. The temperature of the system was maintained by a thermostatic water circulator (JULABO) within ± 0.1 °C. The pressure was indicated by a digital pressure indicator (Druck DPI 150) with a precision of ± 1.0 kPa for a range of (0 to 10 000) kPa. The temperature of the mixing vessel, gas phase, and liquid phase inside the equilibrium cell was measured with a digital thermometer (YOKOGAWA 7653) with a precision of ± 0.01 °C. When the total pressure of the system reaches a constant value and was maintained for at least 2 h, then the equilibrium was assumed to be attained. Liquid samples were withdrawn from the equilibrium cell and analyzed by the titration method[11] to determine the concentration of CO_2 in the liquid phase. The composition of gases after the absorption was determined through online gas chromatography (Perkin-Elmer 5000 GC). A schematic diagram of the SOLTEQ BP-22 high-pressure solubility cell used in the present study is shown in Figure 1.

Table 1. Densities of Aqueous Sodium Glycinate Solutions

	$\rho/g\cdot cm^{-3}$					
T/K	1 % wt	5 % wt	10 % wt	15 % wt	20 % wt	30 % wt
			Present Study			
298.15	1.01196	1.01592	1.03452	1.05560	1.08352	1.13040
313.15	1.00200	1.01056	1.02968	1.04832	1.07644	1.11800
323.15	0.99940	1.00512	1.02256	1.04292	1.07100	1.11276
333.15	0.99672	1.00012	1.01756	1.03672	1.06648	1.10748
343.15	0.99016	0.99324	1.01076	1.03008	1.06120	1.10144
353.15	0.98536	0.98720	1.00532	1.02364	1.05448	1.09452
			Lee et al. (2005)			
303.15	–	–	1.0332	–	1.0800	1.1214
313.15	–	–	1.0296	–	1.0763	1.1176
323.15	–	–	1.0252	–	1.0718	1.1129
333.15	–	–	1.0201	–	1.0665	1.1075
343.15	–	–	1.0145	–	1.0607	1.1015
353.15	–	–	1.0082	–	1.0542	1.0947

Table 2. Correlation Coefficients and SD for Equation 1

% wt	A_0	A_1	R^2	SD
1	−0.00046	1.14788	0.97979	0.00124
5	−0.00053	1.17570	0.98762	0.00111
10	−0.00055	1.20003	0.98864	0.00108
15	−0.00059	1.23130	0.99549	0.00155
20	−0.00052	1.23901	0.99643	0.00057
30	−0.00063	1.31646	0.99327	0.00108

Results and Discussion

A. Density before CO_2 Absorption. The present experimental data on density of aqueous sodium glycinate solutions with a comparison of previously published data[8] are presented in Table 1. Effect of temperature on the density of aqueous sodium glycinate solutions could be represented by the following equation[10]

$$\rho = A_0 T + A_1 \qquad (1)$$

where ρ is the density in $g\cdot cm^{-3}$; T is temperature in K; and A_0 and A_1 are the correlation constants. Standard deviation (SD) of the data was calculated by the following equation[12]

$$\mathrm{SD} = \left(\frac{\sum_{1}^{n} (X_{\mathrm{exp}} - X_{\mathrm{cal}})^2}{n} \right)^{0.5} \qquad (2)$$

where X_{exp}, X_{cal}, and n are the measured experimental values, calculated values using the equations, and the number of measurements made. It was found that densities of aqueous solutions of sodium glycinate increase as the molar concentration increases and decreases with increasing temperature. Figure 2 shows the comparison between the experimental data on density with those calculated from eq 1. The values of correlation constants, R^2, and SD values for eq 1 are presented in Table 2.

B. Solubility of CO_2. To standardize and confirm the reliability and reproducibility of the SOLTEQ BP-22 high pressure solubility cell, 30 % wt MEA solution was used to measure the solubility of CO_2, and the results are compared with the available published data[11,13] on the same pressure range, which are shown in Figure 3. For MEA systems, Shen and Li[11] have used two types of equipment, namely, low-pressure (<) and high-pressure (> 200 KPa). A minor deviation could be attributed to the type of measurements used by the authors,[11] whereas the present

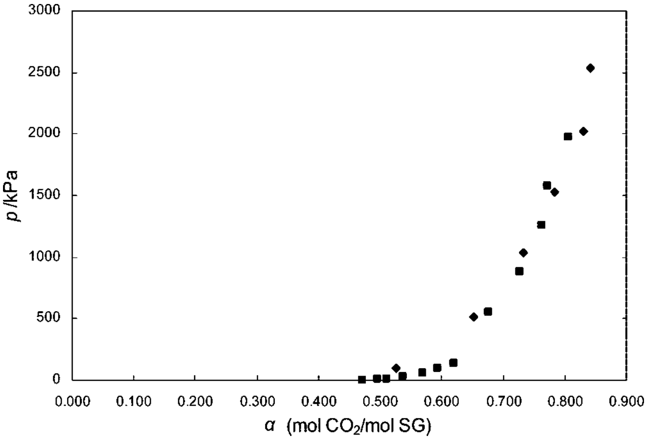

Figure 3. Loading capacity of 30 % wt methyldiethanolamine (MEA) at 313.15 K: ◆, this work; ■, Shen and Li (1992).

Table 3. Solubility of CO_2 in 30 % wt MEA Aqueous Solution at 313.15 K

present work		Shen and Li (1992)	
p/kPa	α	*p*/kPa	α
92	0.526	2.2	0.471
504	0.653	5	0.496
1001	0.734	12.8	0.512
1504	0.784	28.7	0.538
2007	0.830	58.4	0.57
2512	0.842	101.3	0.594
		140.1	0.62
		552	0.676
		883	0.728
		1256	0.763
		1580	0.772
		1973	0.806

Table 4. Solubility of CO_2 in 10 % wt Aqueous Sodium Glycinate Solutions at 313.15 K

present work		Song (2006)	
p/kPa	α	*p*/kPa	α
92	0.888	0.2	0.414
512	1.050	0.4	0.531
1019	1.149	0.9	0.595
1516	1.231	5.7	0.705
2022	1.256	25.2	0.863
2505	1.275	69.5	0.932
		128	1.035
		178	1.048
		208	1.061

Table 5. Densities of Aqueous Sodium Glycinate Solutions before Absorption (ρ_i) and after Absorption (ρ_a) and Solubilities of CO_2 (α = mol CO_2/mol SG)

T = 298.15 K				*T* = 313.15 K			
ρ_i/g·cm^{-3}	*p*/kPa	α	ρ_a/g·cm^{-3}	ρ_i/g·cm^{-3}	*p*/kPa	α	ρ_a/g·cm^{-3}
1 % wt sodium glycinate							
1.01196	98	2.313	1.33538	1.00200	92	2.063	1.33649
	515	2.688	1.33610		528	2.438	1.33864
	1031	3.188	1.33714		995	2.750	1.33894
	1527	3.375	1.33769		1510	2.938	1.33895
	2017	3.563	1.33774		2030	3.125	1.33918
	2535	4.063	1.33853		2483	3.313	1.33967
5 % wt sodium glycinate							
1.01592	98	1.238	1.34013	1.01056	92	1.188	1.34136
	547	1.363	1.34370		514	1.238	1.34263
	1022	1.375	1.34420		1029	1.288	1.34518
	1511	1.438	1.34469		1503	1.338	1.34574
	2020	1.413	1.34517		2007	1.410	1.34605
	2500	1.525	1.34529		2503	1.488	1.34665
10 % wt sodium glycinate							
1.03452	98	0.969	1.34695	1.02968	91	0.888	1.34831
	522	1.156	1.34854		512	1.050	1.34972
	1009	1.281	1.34994		1018	1.150	1.35222
	1517	1.319	1.35340		1515	1.231	1.35430
	2024	1.363	1.35351		2022	1.256	1.35448
	2498	1.431	1.35732		2505	1.275	1.35759
15 % wt sodium glycinate							
1.05560	98	0.929	1.35005	1.04832	91	0.842	1.35605
	526	1.013	1.35799		520	1.029	1.35646
	1002	1.046	1.35800		1017	1.067	1.35829
	1536	1.054	1.35820		1504	1.083	1.35941
	2035	1.113	1.35856		2038	1.142	1.35955
	2521	1.138	1.35975		2499	1.175	1.36023
20 % wt sodium glycinate							
1.08352	98	0.703	1.35220	1.07644	90	0.681	1.35969
	528	0.941	1.35609		508	0.913	1.36520
	1010	0.991	1.36843		1009	1.000	1.36945
	1541	1.022	1.36853		1516	1.031	1.37061
	2038	1.116	1.37229		2019	1.075	1.37446
	2531	1.134	1.37498		2513	1.131	1.37626
30 % wt sodium glycinate							
1.13040	98	0.623	1.37842	1.11800	91	0.575	1.37670
	516	0.906	1.38046		508	0.867	1.37959
	1026	0.958	1.38128		1011	0.954	1.38072
	1526	0.967	1.38267		1525	0.975	1.38437
	2049	0.985	1.38407		2003	0.979	1.38488
	2534	1.031	1.38733		2501	0.988	1.38819

study involves the high-pressure solubility cell. For better comparison, the data are shown in Table 3. Solubility measurements with sodium glycinate were made with the experimental setup for the high-pressure range. The measured value of solubility of carbon dioxide in aqueous solutions of sodium glycinate are estimated as the loading capacity (α = mol CO_2/mol SG) for the temperatures (298.15 and 313.15) K and presented in Table 5. The data are shown in Figures 4 and 5 for the temperatures (298.15 and 313.15) K, respectively. It was observed that loading capacity increases with an increase in partial pressure of CO_2 but decreases with an increase in sodium glycinate concentration. The total absorbed CO_2 per volume of solution was actually increased with an increase in concentration. This can be observed from Figure 5, at pressure 1000 kPa and $T = 313.15$ K. The loading factors for (1, 5, and 10) % wt of sodium glycinate solution are 2.750, 1.288, and 1.150, respectively, but the net CO_2 absorbed in these solutions is (0.282, 0.662, and 1.181) mol·dm^{-3}. The loading capacity of aqueous sodium glycinate (10 % wt) at 313.15 K is compared with those of Song et. al[9] in Figure 6, and the data are given in Table 4.

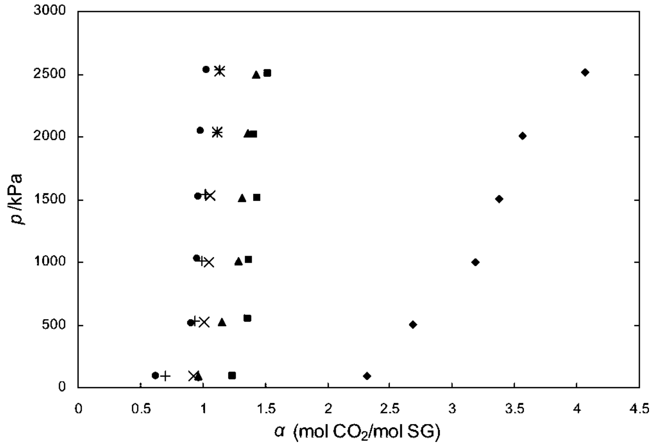

Figure 4. Loading capacity of aqueous sodium glycinate (SG) at 298.15 K; ◆, 1 % wt; ■, 5 % wt; ▲, 10 % wt; ×, 15 % wt; +, 20 % wt; ●, 30 % wt.

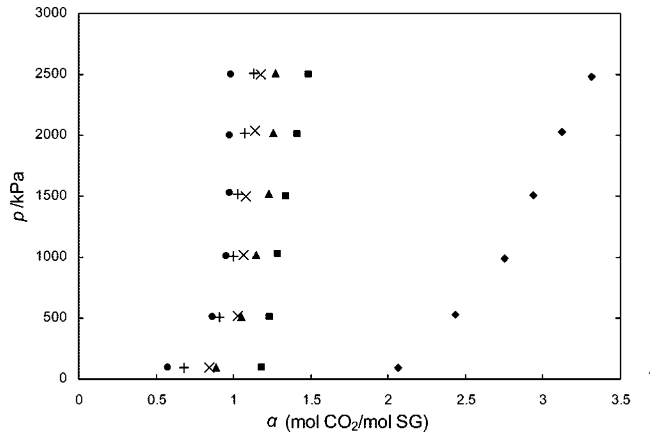

Figure 5. Loading capacity of aqueous sodium glycinate (SG) at 313.15 K; ◆, 1 % wt; ■, 5 % wt; ▲, 10 % wt; ×, 15 % wt; +, 20 % wt; ●, 30 % wt.

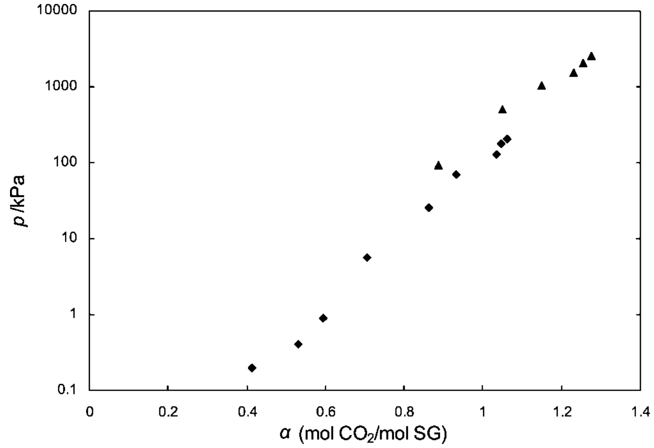

Figure 6. Loading capacity of 10 % wt aqueous sodium glycinate (SG) at 313.15 K; ◆, Song (2006); ▲, this work.

CO_2 absorption using amino acid salt was categorized as an exothermic chemical reaction. According to Le Chatelier principle, increase of temperature would decrease the extent of reaction for this absorption. The results agree with this theory: as the temperature increases, the solubility decreases in the range of pressures studied. Present data on solubility represented as loading capacity are compared with those of published data[9] in Figure 6, which shows a fair degree of comparison.

C. Density after CO_2 Absorption. To account for changes in the densities of aqueous sodium glycinate solutions, density measurements were made after CO_2 absorption at the same condition of absorption. Density values after CO_2 absorption are compared with those before absorption and presented in Table 5, along with temperature and pressure. The densities of aqueous sodium glycinate after absorption give a higher value compared to the density before absorption and increase with an increase in pressure. The amount of CO_2 absorbed was dependent on the partial pressure of CO_2.

Conclusion

In this present work, it was found that densities of aqueous solutions of sodium glycinate increase as the molar concentration increase and decrease with an increase in temperature. The CO_2 solubility increases with an increase in CO_2 partial pressure and decreases with an increase in sodium glycinate concentration and temperature. The densities of aqueous sodium glycinate after absorption gave higher values than those before absorption and increase with increasing pressure.

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