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Solubility of Carbon Dioxide in Aqueous Potassium Salts of Glycine and Taurine at Absorber and Desorber Conditions

Nick Aldenkamp,*,[†] Patrick Huttenhuis,[†] Nathalie Penders-van Elk,[†] Espen Steinseth Hamborg,[‡] and Geert F. Versteeg[†]

[†]Procede Group B.V., Vlierstraat 111, Enschede, 7544 GG The Netherlands
[‡]Statoil Research Centre, Porsgrunn, NO-3908 Norway

ABSTRACT: In this work the vapor liquid equilibria (VLE) of carbon dioxide in both taurine (KTaurate) and glycine (KGlycinate) potassium salts are measured and compared to literature data. The VLE data were measured at two salt concentrations of approximately (1 and 1.8) mol·kg^{-1}, and at temperatures of (313, 333, 353, 373, and 393) K. The experiments were carried out in three different stirred cell reactors, all operated in batch mode to ensure the highest accuracy. The experimental results show that the CO_2 partial pressure for the same loading is higher in all cases for KTaurate compared to KGlycinate. Experiments showed higher acid gas partial pressures for higher concentrations at the same temperature. Furthermore, for both solvents at 373 K the relative difference in CO_2 partial pressure is greatest with a factor 2 for two solutions with the same loading. KGlycinate at 393 K showed significant degradation observed through color change and formation of gas with approximately 3 % AAS conversion in 2.5 days for a concentration of 1.7 mol·kg^{-1}.
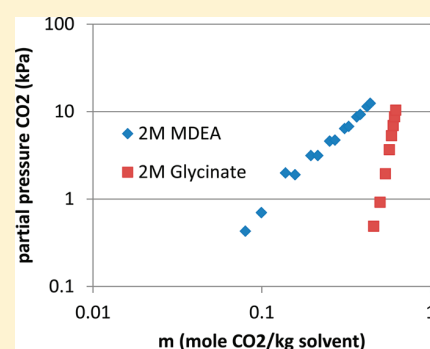
INTRODUCTION

Absorption of CO_2 and other acid gases in alkaline solutions is a widely used industrial process for the treatment of gas streams.[1] Most commonly used solvents are alkanolamines, but major drawbacks are flooding, volatility, foaming, and solvent degradation. Amino acid salt (AAS) solutions gained interest as absorption liquid because of their low volatility, high biodegradability, resistance against oxidation, and thermal stability. Researchers have investigated several types of AAS for kinetic data, stability and proposed AAS processes,[2−4] and in industry, Siemens proposed the PostCap process.[5] The AAS of both Taurine (Taurate) and Glycine (Glycinate) seem promising candidates.[6,7] Above critical crystallization points precipitation can occur,[8] and TNO (Dutch Organization for Applied Scientific Research) applied this in the patented DECAB process concept.[9] For optimal design of AAS processes chemical absorption data is needed. In this work the vapor liquid equilibria (VLE) have been measured for two concentrations of KTaurate and KGlycinate below the precipitation point at both absorber and desorber temperatures and the results were compared to literature data.

EXPERIMENTAL SECTION

Experimental Set-Ups. Two different types of experimental set-ups were used in this project. For the experiments carried out at temperatures of (313, 333, and 353) K, the double cell set-ups (short DB) (shown in Figure 1) were used (where the reactors were submerged in a water bath to ensure uniform temperature). For the experiments at (373 and 393) K, the Buchi Stirred Cell (short SC and shown in Figure 2) was

used heated by an oil bath. All set-ups are validated for VLE by comparing measurements with a 2 mol·kg^{-1} MDEA solution at 313 K with literature data.[10−14] Table 1 summarizes the equipment details.

Chemicals. MDEA (purity > 99 %), Taurine (purity > 98 %), Glycine (purity ∼ 98.5 %) were obtained from Sigma-Aldrich and potassium hydroxide (purity ∼ 90 %) from PPC. Purity of potassium hydroxide is determined by titrating potassium hydroxide solution with 1 M HCl. Carbon dioxide with purity of 99.9998 % was supplied by Air Liquide. Amino acid salts (AAS) of taurine and glycine are made by reacting equimolar amounts of potassium hydroxide in deionized water with their perspective amino acid salt to obtain a clear liquid with a pH in the range 10.5−11.[8]

Experimental Procedures. The aqueous solvent was fed into the reactor for each solubility experiment. Next, the solvent was carefully degassed by applying a deep vacuum to the reactor for short periods of time. Then the reactor was allowed to equilibrate at the desired temperature. At attainment of equilibrium, which is a constant pressure for at least 30 min, the solution's vapor pressure was recorded.

Further, a specified amount of carbon dioxide was fed from the gas supply vessel to the reactor. By recording the pressure and the temperature in the gas supply system before and after addition to the reactor, the amount of CO_2 added to the reactor
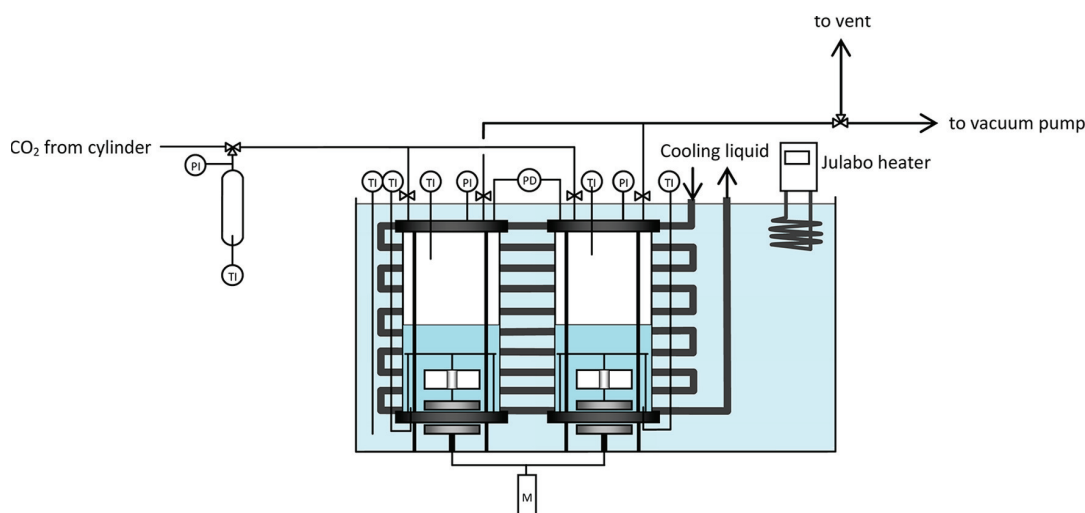
Figure 1. Schematic drawing for the double cell (DB) setup. PI = pressure indicator, TI = temperature meter, M = mixer, PD = (optional) pressure difference meter.
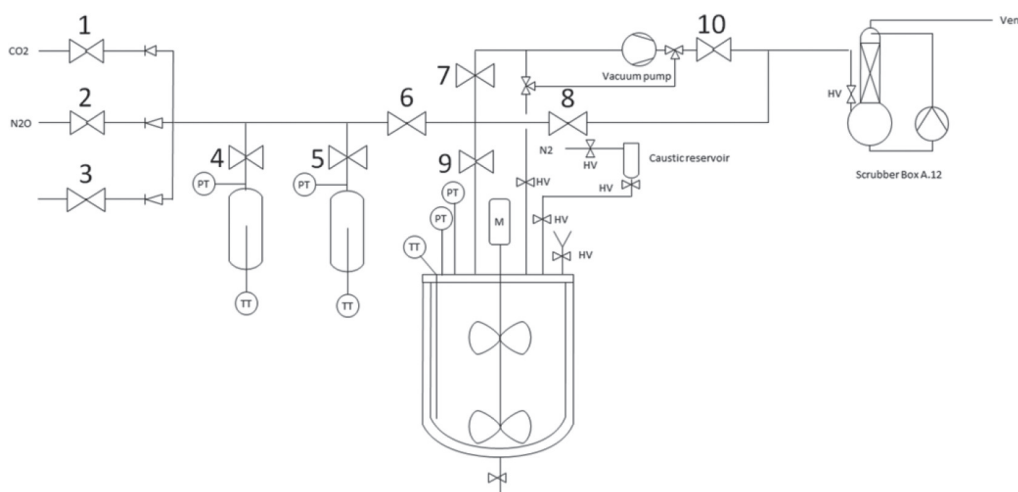

Figure 2. Schematic drawing for the stirred cell (SC) setup. PT = pressure meter, TT = temperature meter, M = mixer, HV = hand valve, numbers 1 to 10 are automated valves, CO_2 and N_2O are connections to CO_2 and N_2O supply vessels, respectively. Note: in this experiments both the caustic vessel and the N_2O connection were not in use.

Table 1. Equipment Details

property (unit)	DB-2	DB-3	SC
V reactor (m^3)	$1.418 \cdot 10^{-3}$	$1.397 \cdot 10^{-3}$	$1.342 \cdot 10^{-3}$
V gas supply (m^3)	$0.411 \cdot 10^{-3}$	$0.377 \cdot 10^{-3}$	$0.691 \cdot 10^{-3}$
P-meter reactor (range in kPa)	Endress Hauser PMP71 (0−400)	Ashcroft Inc. A2ZDM (0−250)	Rosemount 2088 (0−400)
P-meter gas supply (range in kPa)	Endress Hauser (0−1000)	Ashcroft Inc. (0−1000)	Rosemount 2088 (0−1000)
P difference meter (range in kPa)	Endress Hauser PMD75 (0−10)		

was calculated. A correction is made for the compressibility using eq 1:

$$n_{CO_2} = \frac{V_{gasvessel}}{R} \left(\frac{P^0}{T^0 Z^0} - \frac{P^1}{T^1 Z^1} \right) \quad (1)$$

where n_{CO_2} is the amount of moles CO_2 added. $V_{gasvessel}$ is the volume of the gas vessel, R is the gas constant with a value of 8.314 $J \cdot K^{-1} \cdot mol^{-1}$, T is temperature, p is pressure, and z is compressibility factor

Next, the stirrer in the reactor was switched on and the chemical reactions start toward equilibrium. At attainment of equilibrium, the temperature and the pressure in the reactor were recorded. The carbon dioxide solubility at the specified conditions can be calculated from the recorded pressures and temperatures. To determine the amount of gas in the liquid phase the density of the solvent must be known. Therefore, this was measured for both concentrations of each AAS in a temperature range from 283 to 363 K and were the densities for higher temperatures extrapolated from a second degree

Table 2. Densities of Two Molalities KGlycinate and KTaurate for Temperatures from (283 to 393) K[a]

KGlycinate					KTaurate				
$m/\text{mol·kg}^{-1}$	$u/\text{mol·kg}^{-1}$	T/K	$\rho/\text{kg·m}^{-3}$	$u/\text{kg·m}^{-3}$	$m/\text{mol·kg}^{-1}$	$u/\text{mol·kg}^{-1}$	T/K	$\rho/\text{kg·m}^{-3}$	$u/\text{kg·m}^{-3}$
0.99	0.035	293	1065	53	0.89	0.031	283	1084	54
0.99	0.035	298	1064	53	0.89	0.031	288	1083	54
0.99	0.035	303	1062	53	0.89	0.031	293	1081	54
0.99	0.035	308	1060	53	0.89	0.031	298	1079	54
0.99	0.035	313	1058	53	0.89	0.031	303	1078	54
0.99	0.035	318	1056	53	0.89	0.031	308	1076	54
0.99	0.035	323	1053	53	0.89	0.031	313	1073	54
0.99	0.035	328	1051	53	0.89	0.031	318	1071	54
0.99	0.035	333	1048	52	0.89	0.031	323	1069	53
0.99	0.035	338	1045	52	0.89	0.031	328	1066	53
0.99	0.035	343	1042	52	0.89	0.031	333	1064	53
0.99	0.035	348	1039	52	0.89	0.031	338	1061	53
0.99	0.035	353	1036	52	0.89	0.031	343	1058	53
0.99	0.035	358	1033	52	0.89	0.031	353	1051	53*
0.99	0.035	363	1030	52	0.89	0.031	373	1037	52*
0.99	0.035	373	1023	51*	0.89	0.031	393	1021	51*
0.99	0.035	393	1007	50*	1.60	0.056	293	1145	57
1.78	0.062	293	1130	57	1.60	0.056	298	1143	57
1.78	0.062	298	1128	56	1.60	0.056	303	1141	57
1.78	0.062	303	1126	56	1.60	0.056	308	1139	57
1.78	0.062	308	1124	56	1.60	0.056	313	1136	57
1.78	0.062	313	1121	56	1.60	0.056	318	1134	57
1.78	0.062	318	1119	56	1.60	0.056	323	1131	57
1.78	0.062	323	1116	56	1.60	0.056	328	1129	56
1.78	0.062	328	1114	56	1.60	0.056	333	1126	56
1.78	0.062	333	1111	56	1.60	0.056	338	1123	56
1.78	0.062	338	1108	55	1.60	0.056	343	1120	56
1.78	0.062	343	1105	55	1.60	0.056	348	1117	56
1.78	0.062	348	1102	55	1.60	0.056	353	1114	56
1.78	0.062	353	1099	55	1.60	0.056	358	1111	56
1.78	0.062	358	1096	55	1.60	0.056	363	1108	55
1.78	0.062	363	1093	55	1.60	0.056	373	1101	55*
1.78	0.062	373	1086	54*	1.60	0.056	393	1086	54*
1.78	0.062	393	1071	54*					

[a]Values denoted with * are extrapolated from a polynomial plot through the data points).

polynomial fit through the data points. Increases in density or volume due to absorption of CO_2 in the liquid during the experiments were considered negligible.

The CO_2 partial pressure (P_{CO2}) is calculated from the difference between the initial solution's vapor pressure (P_{vapor}) and the reactor pressure at equilibrium after CO_2 addition ($P_{Reactor}$) via eq 2:

$$P_{CO_2} = P_{Reactor} - P_{vapor} \tag{2}$$

For the experiments at 353 K the value of the pressure difference meter was used. Small fluctuations in temperature influence the total pressure due to substantial variations in water vapor pressure. When both reactors are filled with the same concentration of AAS, pressure differences are leveled out and a pressure difference meter is used to measure the net CO_2 pressure. Then, the CO_2 pressure is the value shown by the pressure difference meter.

Sample Analysis. Samples of unloaded and loaded solutions from the experiments were titrated with 1 N HCl using a Metrohm 716 DMS Titrino to validate the weighing of the taurate and glycinate, as well as to check for possible loss of water during vacuuming. When multiple equivalence points were found, the one around pH 4 was chosen because this gives

the value for all free AAS and all reaction products in the solution. Second, in eq 3 the value for the amino acid concentration (C_AAS) was corrected for the amount of CO_2 absorbed during the experiment.

$$C\_AAS = C\_AAS, \text{measured}$$
$$\frac{\text{mass}_{\text{liquid}\rightarrow\text{reactor}} + \text{mass}_{CO2,\text{gas added}}}{\text{mass}_{\text{liquid}\rightarrow\text{reactor}}} \tag{3}$$

C_AAS,measured is the density measured from the loaded solution. The density of the unloaded solution was measured using an Anton Paar DMA 4500 M density meter and is tabulated in Table 2.

■ RESULTS AND DISCUSSION OF VLE EXPERIMENTS

The results of the validation experiments through the absorption of CO_2 in approximately 2 mol·kg^{-1} MDEA are presented in Figure 3 and Figure 4 for the DB set-ups and the SC, respectively. Both axes are in logarithmic scale; the x-axis shows the loading in mole CO_2 per mol of MDEA and on the y-axis gives the partial pressure of CO_2. In Figure 4, it is shown that the measured CO_2 partial pressure for the SC setup for the
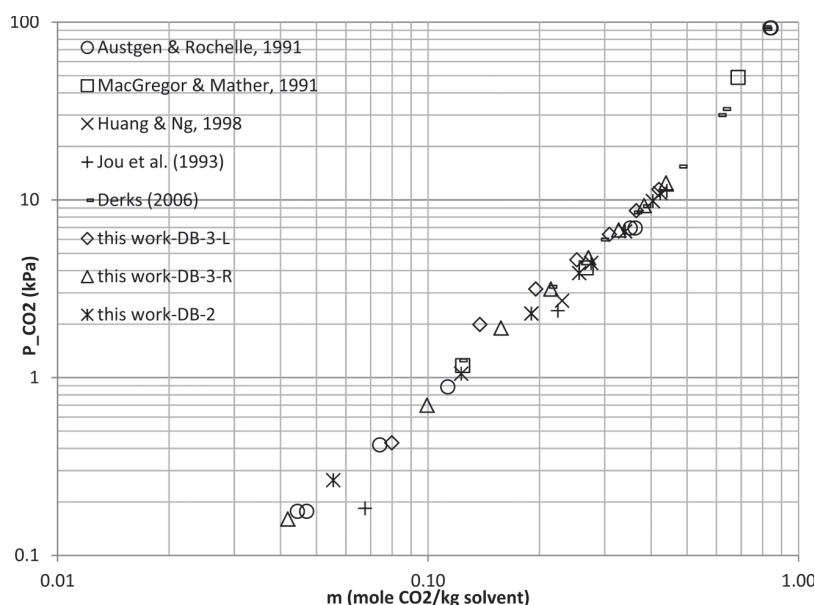
Figure 3. Validation plot for the DB set-ups with data of CO_2 absorption in 2 mol·kg^{-1} MDEA at 313 K compared with literature data[10−14]
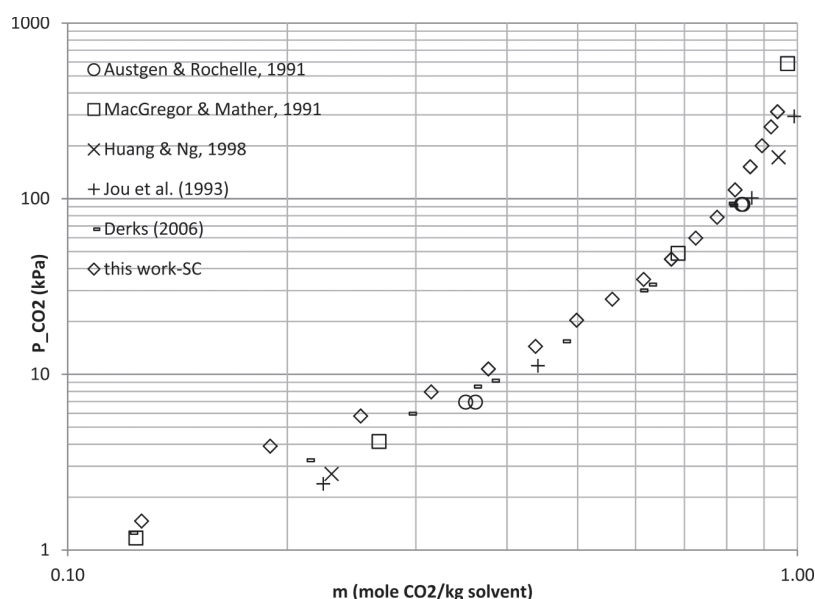

Figure 4. Validation plot for the SC setup with data of CO_2 absorption in 2 mol·kg^{-1} MDEA compared with literature data[10−14]

pressure region of interest, 10−100 kPa, were in line with literature.

In Figure 5 the results of VLE experiments are shown for KGlycinate and Figure 6 shows the values for KTaurate. The data points for these graphs are tabulated in Tables 3 to 11. The x-axis shows the loading as mol CO_2/mol taurate or glycinate on a logarithmic scale. On the y-axis the partial pressure of CO_2 is shown in kPa, also on logarithmic scale.

Comparing Figures 5 and 6 shows that glycinate solutions have a lower CO_2 partial pressure and therefore higher capacity than Ktaurate at similar CO_2 loadings for all temperatures. In Figure 7 experimental data at (1 and 1.7) mol·kg^{-1} Glycinate at 313 K from this work is compared to the KGlycinate data of Portugal[6] and the NaGlycinate data of Song.[15] The CO_2 partial pressure for NaGlycinate compared to KGlycinate shows that

NaGlycinate seems to have lower CO_2 partial pressures for the same loading. On the other hand, Portugal has measured significantly lower partial pressures for the KGlycinate system at 1 mol·kg^{-1}.

For KGlycinate solutions at temperatures of (313, 353, and 373) K, the partial pressure of CO_2 is significantly higher for more concentrated solutions. The exception is the experiment of 333 K. The effect that more concentrated solutions give higher partial pressures for the same loading was also observed by Song et al. in their work on absorption of CO_2 in Na-Glycinate at temperatures from (303.15 to 323.15) K.[15] For all KTaurate experiments except at 353 K this behavior was observed to a lesser extent than for KGlycinate. For both AAS at 373 K the difference in partial pressure between high, 1.7 mol·kg^{-1}, and low, 1.0 mol·kg^{-1}, concentration is the highest by
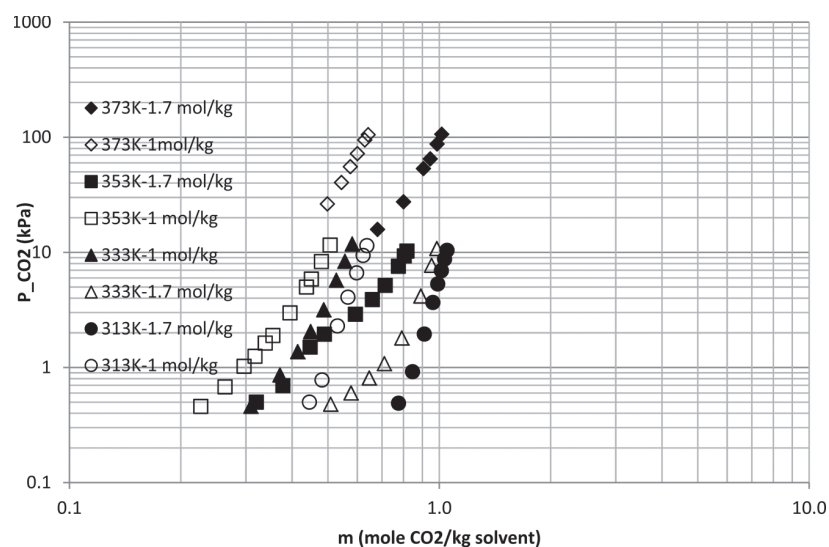
Figure 5. Partial pressure of CO_2 in KGlycinate solutions for temperatures of (313 to 373) K. The x-axis shows the molality of CO_2 per kg solvent. The y-axis gives the partial pressure of CO_2 in kPa.
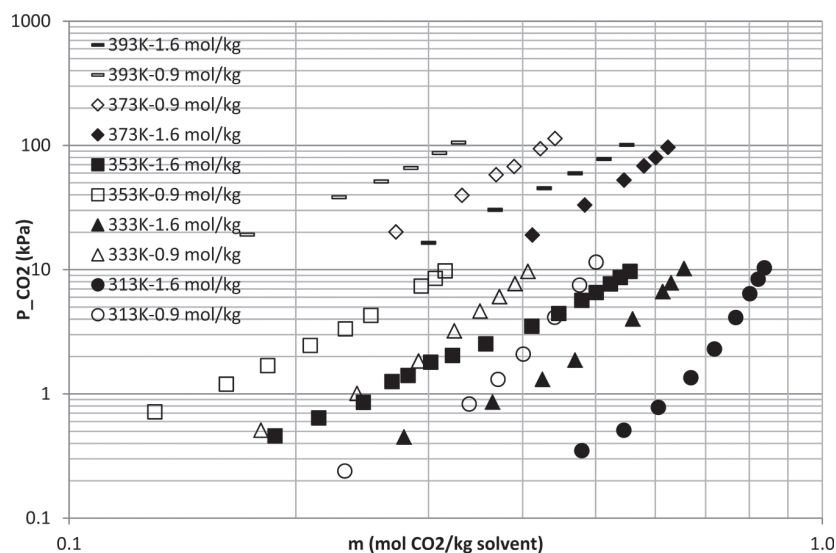

Figure 6. Partial pressure of CO_2 in KTaurate solutions at temperatures from (313 to 393) K. The x-axis shows the molality of CO_2 per kg solvent. The y-axis gives the partial pressure of CO_2 in kPa.

Table 3. VLE Data Points for KGlycinate Experiments at 313 K[a]

m AAS = 0.953 mol·kg⁻¹				m AAS = 1.689 mol·kg⁻¹			
m CO_2	u CO_2	P_CO_2	u CO_2	m CO_2	u CO_2	P_CO_2	u CO_2
mol·kg⁻¹	mol·kg⁻¹	kPa	kPa	mol·kg⁻¹	mol·kg⁻¹	kPa	kPa
0.4452	0.0134	0.5	0.025	0.7755	0.0233	0.49	0.025
0.4815	0.0144	0.78	0.025	0.8460	0.0254	0.92	0.025
0.5299	0.0159	2.3	0.025	0.9103	0.0273	1.95	0.025
0.5657	0.0170	4.09	0.025	0.9599	0.0288	3.67	0.025
0.5973	0.0179	6.64	0.025	0.9893	0.0297	5.32	0.025
0.6220	0.0187	9.41	0.025	1.0123	0.0304	6.95	0.025
0.6366	0.0191	11.45	0.025	1.0324	0.0310	8.75	0.025
				1.0486	0.0315	10.41	0.025

[a]The m AAS is the molality the solvent in mol·kg⁻¹, m CO_2 is molality in mol CO_2/kg solvent, u CO_2 the uncertainty in mol·kg⁻¹, P_CO_2 is the partial pressure of CO_2 above the solvent in kPa, u the uncertainty in kPa.

Table 4. VLE Data Points for KGlycinate Experiments at 333 K[a]

	m AAS = 1.001 mol·kg⁻¹				m AAS = 1.761 mol·kg⁻¹		
m CO₂	u CO₂	P_CO₂	u CO₂	m CO₂	u CO₂	P_CO₂	u CO₂
mol·kg⁻¹	mol·kg⁻¹	kPa	kPa	mol·kg⁻¹	mol·kg⁻¹	kPa	kPa
0.3092	0.0093	0.46	0.025	0.5081	0.0152	0.48	0.025
0.3707	0.0111	0.86	0.025	0.5772	0.0173	0.6	0.025
0.4140	0.0124	1.37	0.025	0.6466	0.0194	0.81	0.025
0.4488	0.0135	2.05	0.025	0.7098	0.0213	1.08	0.025
0.4870	0.0146	3.17	0.025	0.7913	0.0237	1.8	0.025
0.5267	0.0158	5.72	0.025	0.8908	0.0267	4.17	0.025
0.5555	0.0167	8.36	0.025	0.9526	0.0286	7.72	0.025
0.5814	0.0174	11.8	0.025	0.9847	0.0295	10.8	0.025

[a]The m AAS is the molality the solvent in mol·kg⁻¹, m CO₂ is molality in mol CO₂/kg solvent, u CO₂ the uncertainty in mol·kg⁻¹, P_CO₂ is the partial pressure of CO₂ above the solvent in kPa, u the uncertainty in kPa.

Table 5. VLE Data Points for KGlycinate Experiments at 353 K[a]

	m AAS = 0.984 mol·kg⁻¹				m AAS = 1.783 mol·kg⁻¹		
m CO₂	u CO₂	P_CO₂	u CO₂	m CO₂	u CO₂	P_CO₂	u CO₂
mol·kg⁻¹	mol·kg⁻¹	kPa	kPa	mol·kg⁻¹	mol·kg⁻¹	kPa	kPa
0.2264	0.0068	0.46	0.025	0.3200	0.0096	0.501	0.025
0.2632	0.0079	0.68	0.025	0.3776	0.0113	0.697	0.025
0.2965	0.0089	1.026	0.025	0.4471	0.0134	1.507	0.025
0.3172	0.0095	1.253	0.025	0.4886	0.0147	1.947	0.025
0.3381	0.0101	1.63	0.025	0.5929	0.0178	2.904	0.025
0.3548	0.0106	1.9	0.025	0.6589	0.0198	3.888	0.025
0.3943	0.0118	2.985	0.025	0.7139	0.0214	5.172	0.025
0.4372	0.0131	5	0.025	0.7748	0.0232	7.575	0.025
0.4508	0.0135	5.872	0.025	0.8036	0.0241	9.305	0.025
0.4798	0.0144	8.33	0.025	0.8171	0.0245	10.275	0.025
0.5064	0.0152	11.583	0.025				

[a]The m AAS is the molality the solvent in mol·kg⁻¹, m CO₂ is molality in mol CO₂/kg solvent, u CO₂ the uncertainty in mol·kg⁻¹, P_CO₂ is the partial pressure of CO₂ above the solvent in kPa, u the uncertainty in kPa.

Table 6. VLE Data Points for KGlycinate Experiments 373 K[a]

	m AAS = 1.024 mol·kg⁻¹				m AAS = 1.843 mol·kg⁻¹		
m CO₂	u CO₂	P_CO₂	u CO₂	m CO₂	u CO₂	P_CO₂	u CO₂
mol·kg⁻¹	mol·kg⁻¹	kPa	kPa	mol·kg⁻¹	mol·kg⁻¹	kPa	kPa
0.4981	0.0149	26.32	0.5	0.6804	0.0204	15.83	0.5
0.5438	0.0163	40.5	0.5	0.7999	0.0240	27.47	0.5
0.5745	0.0172	55.52	0.5	0.9057	0.0272	53.41	0.5
0.6005	0.0180	72.02	0.5	0.9449	0.0283	64.84	0.5
0.6286	0.0189	94.69	0.5	0.9860	0.0296	87.27	0.5
0.6423	0.0193	105.1	0.5	1.0150	0.0305	106.22	0.5

[a]The m AAS is the molality the solvent in mol·kg⁻¹, m CO₂ is molality in mol CO₂/kg solvent, u CO₂ the uncertainty in mol·kg⁻¹, P_CO₂ is the partial pressure of CO₂ above the solvent in kPa, u the uncertainty in kPa.

approximately a factor 2, while for the KTaurate experiment this increase in difference seems absent with only differences around 10 kPa for the same loading and high and low concentration.

Portugal[6] measured VLE of CO₂ in 1 mol·kg⁻¹ KGlycinate solutions and found for experiments at 313 K lower CO₂ pressures for all loadings when compared to this work. This is in contradiction with experiments at 353 K which showed higher CO₂ partial pressures for loadings up to 0.4 mol/mol and higher values for loadings higher than 0.4 mol/mol (see Figure 8). It is not clear what causes this discrepancy in results, because additional data of this system are not available in the literature. Since the general trend for all measurements of

partial pressure versus CO₂ loading in amine systems result in a straight line when plotting on a log/log scale it is anticipated that the values for Portugal[6] up to 0.4 mol/mol are too high.

Comparison of present KTaurate VLE to the work of Kumar[8] in Figure 9 clearly shows that Kumar measured substantially higher CO₂ pressures for the same loading, even when comparing Kumar's 1 mol·kg⁻¹ result to the 1.6 mol·kg⁻¹ from this present work. Possible cause for this discrepancy might be the continuous supply technique used by Kumar to obtain the VLE data. Kumar continuously supplied a diluted (< 6 vol % CO₂ in a CO₂/N₂ mixture) gas stream to a stirred cell until equilibrium was achieved and measured the CO₂ pressure based on the CO₂ concentration in the gas phase of the reactor.

Table 7. VLE Data Points for KTaurate Experiments at 313 K[a]

m AAS = 0.873 mol·kg^{-1}				m AAS = 1.553 mol·kg^{-1}			
m CO$_2$	u CO$_2$	P_CO$_2$	u CO$_2$	m CO$_2$	u CO$_2$	P_CO$_2$	u CO$_2$
mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	mol·kg^{-1}	mol·kg^{-1}	kPa	kPa
0.2322	0.0070	0.24	0.025	0.4793	0.0144	0.35	0.025
0.3397	0.0102	0.83	0.025	0.5449	0.0163	0.51	0.025
0.3709	0.0111	1.31	0.025	0.6056	0.0182	0.78	0.025
0.4008	0.0120	2.09	0.025	0.6689	0.0201	1.35	0.025
0.4411	0.0132	4.14	0.025	0.7189	0.0216	2.3	0.025
0.4759	0.0143	7.52	0.025	0.7673	0.0230	4.12	0.025
0.5007	0.0150	11.51	0.025	0.8009	0.0240	6.41	0.025
				0.8215	0.0246	8.4	0.025
				0.8372	0.0251	10.36	0.025

[a]The m AAS is the molality the solvent in mol·kg^{-1}, m CO$_2$ is molality in mol CO$_2$/kg solvent, u CO$_2$ the uncertainty in mol·kg^{-1}, P_CO$_2$ is the partial pressure of CO$_2$ above the solvent in kPa, u the uncertainty in kPa.

Table 8. VLE Data Points for KTaurate Experiments at 333 K[a]

m AAS = 0.904 mol·kg^{-1}				m AAS = 1.555 mol·kg^{-1}			
m CO$_2$	u CO$_2$	P_CO$_2$	u CO$_2$	m CO$_2$	u CO$_2$	P_CO$_2$	u CO$_2$
mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	mol·kg^{-1}	mol·kg^{-1}	kPa	kPa
0.1797	0.0054	0.51	0.025	0.2783	0.0083	0.45	0.025
0.2411	0.0072	1.01	0.025	0.3648	0.0109	0.86	0.025
0.2910	0.0087	1.84	0.025	0.4249	0.0127	1.31	0.025
0.3245	0.0097	3.22	0.025	0.4695	0.0141	1.87	0.025
0.3511	0.0105	4.64	0.025	0.5597	0.0168	4.01	0.025
0.3725	0.0112	6.07	0.025	0.6137	0.0184	6.66	0.025
0.3908	0.0117	7.72	0.025	0.6297	0.0189	7.83	0.025
0.4065	0.0122	9.69	0.025	0.6552	0.0197	10.21	0.025

[a]The m AAS is the molality the solvent in mol·kg^{-1}, m CO$_2$ is molality in mol CO$_2$/kg solvent, u CO$_2$ the uncertainty in mol·kg^{-1}, P_CO$_2$ is the partial pressure of CO$_2$ above the solvent in kPa, u the uncertainty in kPa.

Table 9. VLE Data Points for KTaurate Experiments at 353 K[a]

m AAS = 0.884 mol·kg^{-1}				m AAS = 1.583 mol·kg^{-1}			
m CO$_2$	u CO$_2$	P_CO$_2$	u CO$_2$	m CO$_2$	u CO$_2$	P_CO$_2$	u CO$_2$
mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	mol·kg^{-1}	mol·kg^{-1}	kPa	kPa
0.0707	0.0021	0.177	0.025	0.1876	0.0056	0.46	0.025
0.1299	0.0039	0.718	0.025	0.2144	0.0064	0.642	0.025
0.1617	0.0049	1.2	0.025	0.2457	0.0074	0.855	0.025
0.1835	0.0055	1.692	0.025	0.2683	0.0080	1.259	0.025
0.2089	0.0063	2.456	0.025	0.2818	0.0085	1.408	0.025
0.2326	0.0070	3.34	0.025	0.3020	0.0091	1.802	0.025
0.2515	0.0075	4.29	0.025	0.3228	0.0097	2.04	0.025
0.2933	0.0088	7.39	0.025	0.3573	0.0107	2.531	0.025
0.3062	0.0092	8.516	0.025	0.4113	0.0123	3.51	0.025
0.3156	0.0095	9.79	0.025	0.4468	0.0134	4.445	0.025
0.3233	0.0097	10.837	0.025	0.4792	0.0144	5.66	0.025
				0.5008	0.0150	6.55	0.025
				0.5229	0.0157	7.68	0.025
				0.5391	0.0162	8.66	0.025
				0.5554	0.0167	9.687	0.025

[a]The m AAS is the molality the solvent in mol·kg^{-1}, m CO$_2$ is molality in mol CO$_2$/kg solvent, u CO$_2$ the uncertainty in mol·kg^{-1}, P_CO$_2$ is the partial pressure of CO$_2$ above the solvent in kPa, u the uncertainty in kPa.

During the experiments at 393 K for both concentrations of KGlycinate, the solution color changed from a clear liquid to dark brown after adding CO$_2$ and operating at 393 K for more than 24 h. The intensity increased with the residence time which was varied from (1.5 to 2.5) days. The color change was also observed by Erga et al. for desorption experiments at 410 K.[16] Furthermore, two repeated experiments with 1.7 mol·kg^{-1} KGlycinate and loading of approximately 0.1 mol CO$_2$/mol AAS at 393 K showed a steady increase of pressure during preparation and execution of the experiment. The present hypothesis is that the formation of gas as a result of solvent degradation. For example, decarboxylation of the glycinate to

Table 10. VLE Data Points for KTaurate Experiments at 373 K[a]

m AAS = 0.919 mol·kg⁻¹				m AAS = 1.624 mol·kg⁻¹			
m CO_2	u CO_2	P_CO_2	u CO_2	m CO_2	u CO_2	P_CO_2	u CO_2
mol·kg⁻¹	mol·kg⁻¹	kPa	kPa	mol·kg⁻¹	mol·kg⁻¹	kPa	kPa
0.2716	0.0081	20.13	0.5	0.4120	0.0124	19.01	0.5
0.3324	0.0100	39.63	0.5	0.4836	0.0145	33.12	0.5
0.3689	0.0111	58.1	0.5	0.5454	0.0164	52.62	0.5
0.3897	0.0117	67.7	0.5	0.5796	0.0174	68.43	0.5
0.4223	0.0127	93.89	0.5	0.6008	0.0180	79.85	0.5
0.4416	0.0132	113.53	0.5	0.6238	0.0187	96.5	0.5

[a]The m AAS is the molality the solvent in mol·kg⁻¹, m CO_2 is molality in mol CO_2/kg solvent, u CO_2 the uncertainty in mol·kg⁻¹, P_CO_2 is the partial pressure of CO_2 above the solvent in kPa, u the uncertainty in kPa.

Table 11. VLE Data Points for KTaurate Experiments at 393 K[a]

m AAS = 0.912 mol·kg⁻¹				m AAS = 1.617 mol·kg⁻¹			
m CO_2	u CO_2	P_CO_2	u CO_2	m CO_2	u CO_2	P_CO_2	u CO_2
mol·kg⁻¹	mol·kg⁻¹	kPa	kPa	mol·kg⁻¹	mol·kg⁻¹	kPa	kPa
0.1724	0.0052	19.14	0.5	0.3001	0.0090	16.43	0.5
0.2282	0.0068	38.22	0.5	0.3677	0.0110	30.3	0.5
0.2596	0.0078	51.23	0.5	0.4272	0.0128	45.19	0.5
0.2842	0.0085	65.67	0.5	0.4696	0.0141	59.52	0.5
0.3101	0.0093	86.74	0.5	0.5127	0.0154	77.69	0.5
0.3288	0.0099	105.49	0.5	0.5499	0.0165	100.87	0.5

[a]The m AAS is the molality the solvent in mol·kg⁻¹, m CO_2 is molality in mol CO_2/kg solvent, u CO_2 the uncertainty in mol·kg⁻¹, P_CO_2 is the partial pressure of CO_2 above the solvent in kPa, u the uncertainty in kPa.
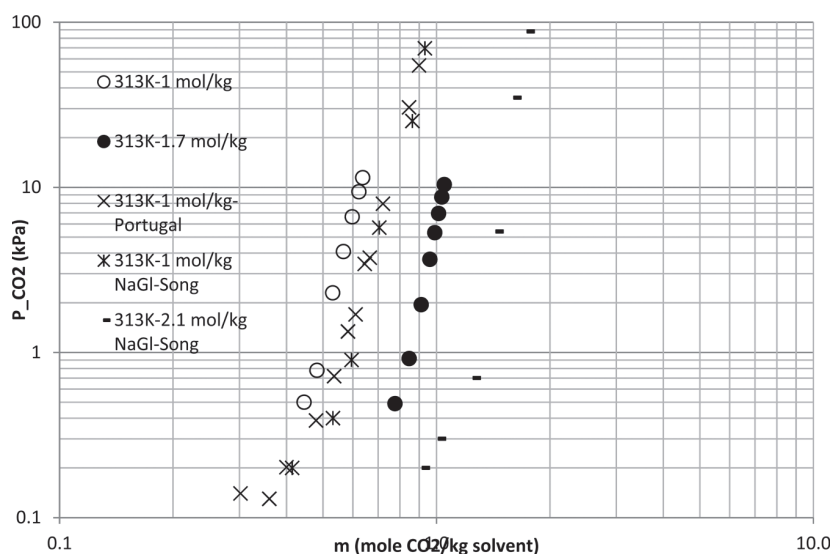

Figure 7. Partial pressure of CO_2 in KGlycinate and NaGlycinate solutions at 313 K. The x-axis shows the molality of CO_2 per kg solvent. The y-axis gives the partial pressure of CO_2 in kPa.

form CO_2 might occur. For the 1.7 mol·kg⁻¹ experiment in approximately 70 h the pressure increased 125 kPa which corresponds to a conversion of around 3 %. This is based on the assumption that the amount of moles produced in the gas phase by using the ideal gas law and assuming that one mole of degradated liquid species forms one mole of gaseous degradation product. For the 1 mol·kg⁻¹ KGlycinate experiment some increases in pressure are larger than expected due to the differences in temperature that were noticed. Since the error in the titration measurements was in the same order of magnitude it was not possible to validate the conversion by measuring a concentration difference after the experiment. In the work of Epp et al.[7] thermal degradation of glycinate is absent. Possible cause might be either the short residence time of 30 min at desorber temperature or the lower regeneration temperature (boiling temperature of 2 mol·kg⁻¹ glycinate solution). Aronu et al.[17] desorbed at a lower temperature of 353 K and noticed no degradation.

■ CONCLUSIONS

VLE data of both KTaurate and KGlycinate solutions were measured for two concentrations of approximately (1 and 1.8)
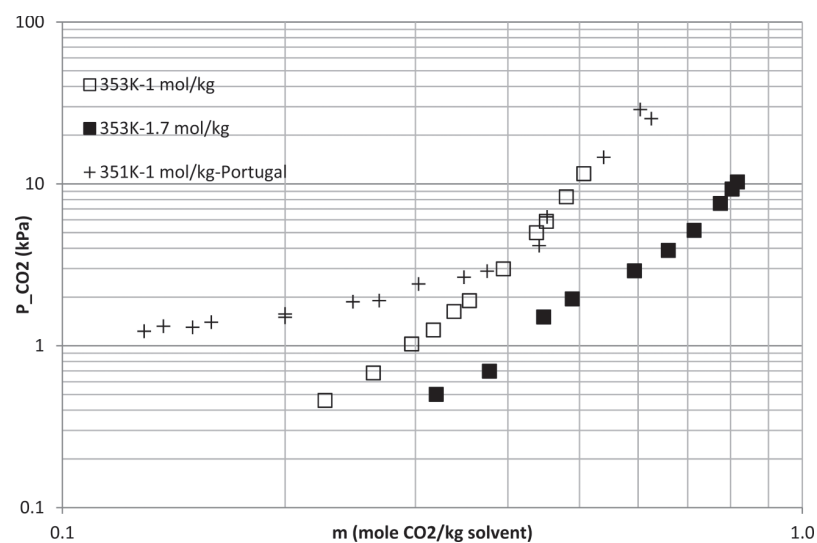
Figure 8. Partial pressure of CO_2 in KGlycinate solutions at 353 K. The x-axis shows the molality of CO_2 per kg solvent. The y-axis gives the partial pressure of CO_2 in kPa.
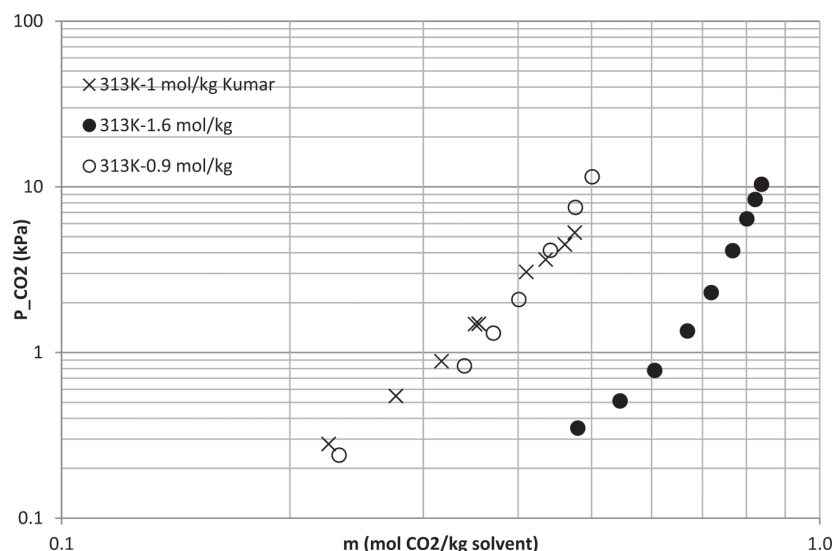

Figure 9. Partial pressure of CO_2 in Ktaurate solutions at 313 K. The x-axis shows the molality of CO_2 per kg solvent. The y-axis gives the partial pressure of CO_2 in kPa.

mol·kg^{-1} and at temperatures of (313, 333, 353, 373, and 393) K. Densities for both AAS were measured for both concentrations at temperatures from (283 to 363) K. KGlycinate showed consistently higher capacity for all measured concentrations and temperatures. Compared to literature data, the results in the present work on values of CO_2 partial pressure vary. For more concentrated solutions, the partial pressure of CO_2 was higher for the same loading in the majority of the experiments, with a maximum difference of a factor 2 for both KGlycinate and KTaurate at a temperature of 373 K. KGlycinate solutions degradate at 393 K and show color change and gas formation.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: nickaldenkamp@gmail.com.

Notes

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■ REFERENCES
(1) Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, 1997.
(2) Lu, J.-G.; Ji, Y.; Zhang, H.; Chen, M. D. CO2 capture using activated amino acid salt solutions in a membrane contactor. *Sep. Sci. Technol.* **2010**, *45*, 1240−1251.
(3) Hamborg, E.; Niederer, J.; Versteeg, G. Dissociation Constants and Thermodynamic Properties of Amino Acids Used in CO2 Absorption from (293 to 353) K. *J. Chem. Eng. Data* **2007**, *52*, 2491−2502.

(4) Holst J. Van Politiek P.; Niederer J.; Versteeg G.; CO2 capture from flue gas using amino acid salt solutions, *GHGT-8 conference*, Trondheim, 2006.

(5) Jockenhövel, T.; Schneider, R. Towards commercial application of a second-generation post-combustion capture technology — Pilot plant validation of the siemens capture process and implementation of a first demonstration case. *Energy Proc.* **2011**, *4*, 1454−1458.

(6) Portugal, A.; Sousa, J.; Magalhaes, F.; Mendes, A. soluibility of carbon dioxide in aqeous solutions of amino acid salts. *Chem. Eng. Sci.* **2009**, *64*, 1993−2002.

(7) Epp, B.; Fahlenkamp, H.; Vogt, M. degradation of solutions of monoethanolamine, diglycolamine and potassium glycinate in view of tauil-end CO2 absorption. *Energy Proc.* **2011**, *4*, 75−80.

(8) Kumar P. S.; Development and design of membrane gas absorption processes, PhD thesis, University of Twente: Enschede, 2002.

(9) Sanchez-Fernandez, E.; de Miguel Mercader, F.; Misiak, K.; van der Ham, L.; Linders, M.; Goetheer, E. New Process concepts for CO2 capture based on precipitating amino acids. *Energy Proc.* **2013**, *37*, 1160−1171.

(10) Austgen, D.; Rochelle, G. model of vapor-liquid equilibria for aqueous acid gasalkanolamine systems. Representation of H2S and CO2 solubility in aqueous MDEA and mixtures of MDEA with MEA or DEA. *Ind. Eng. Chem. Res.* **1991**, *30*, 543−555.

(11) Derks, P.; Carbon dioxide absorption in piperazine activated N-Methyldiethanolamine, University of Twente: Enschede, 2006.

(12) Huang S.; Ng J.; Solubility of H2S and CO2 in Alkanolamines, GPA research report RR-155, DB Robinson Research Ltd., September 1998.

(13) Jou, F.; Caroll, J.; Mather, A.; Otto, F. solubility of mixtures of hydrogen sulfide and carbon dioxide in aqueous N-Methyldiethanolamine solutions. *J. Chem. Eng. Data* **1993**, *38*, 75−77.

(14) Mather, A.; MacGregor, R. Equilibrium Solubility of H2S and CO2 and Their Mixtures in a Mixed Solvent. *Can. J. Chem. Eng.* **1991**, *69*, 1357−1366.

(15) 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.

(16) Erga, O.; Juliussen, O.; Lidal, H. carbon dioxide recovery by means of aqueous amines. *Energy Convers. Mgmt* **1995**, *36*, 387−392.

(17) Aronu, U.; Svendsen, H.; Hoff, K. Investigation of amine amino acid salts for carbon dioxide absorption. *Int. J. Greenhouse Gas Contr.* **2010**, *4*, 771−775.

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