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Calorimetric Studies of Precipitating Solvent System

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Abstract

Calorimetric study of a precipitating solvent system of Potassium-Taurate (KTAU) was performed in the CPA202 calorimeter. Two different experiments were conducted, i.e. heat of absorption of CO₂ in KTAU solvent at different conditions (concentration = 1.5 M and 3.0 M), loading up to ~ 0.8 mol CO₂/ mol Taurine and temperature = 25°C, 40°C, 80°C). Moreover, dissolution heats of Taurine/solid were also measured. The result agrees well with the reported data. The procedure developed for the heat of dissolution measurements was verified by measuring heat of dissolution of solid Taurine in water and comparing results with data in literature. The solid formation occurs during the absorption of CO₂ in 3.0M KTAU at low temperatures (25°C and 40°C) and at loadings (~ 0.3 mol CO₂/ mol Taurine). The heat of dissolution of the formed solid in pure water is slightly higher than that of Taurine in pure water but less heat is required to dissolve the same solids in unloaded 3.0 M KTAU solution.

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1. Introduction

Neutralized amino acid salts could be an attractive alternative to alkanolamines as solvents for CO₂ absorption, due to comparable reactivity and absorption capacity [1-3], better resistance to degradation, negligible volatility and higher surface tension [1] and also a favorable pK_a value [4].

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An amino acid molecule can contain primary or secondary amino-groups, which react with CO₂ similarly to alkanolamines. The main products are carbamate (R1) and bicarbonate (R2).



Solid formations might be observed during the CO₂ absorption with amino-acid salts solutions under certain range of concentrations, temperatures and pH of solutions [1]. Depending on amino acid and process conditions, the solid product may be a neutralized salt of amino acid, amino acid itself, bicarbonate of amino acid or metal bicarbonate. In a standard absorption-desorption process, the solid formation could be a big challenge in the operation but under specific circumstances can turn as advantages to the process, for instance leading to higher CO₂ capacity.

Fernandez et al. [5, 6] have made a conceptual process development by comparing non-precipitating and precipitating systems and reported that the precipitating solvent gave significant reductions in the energy consumption, - 35% compared to a conventional process based on 5M MEA. The energy consumption was estimated based on experimental VLE data. The Van Hoff equation was used to derive the heat absorption of CO₂ into solutions from the VLE correlation. An additional heating source in the form of low quality steam to re-dissolve the solid was also reported to account for about 10 % of the energy requirement. Neither heat of absorption nor heat of dissolution of the solid was measured.

This work aims to provide the experimental data on a calorimetric measurement for both the heat of absorptions of CO₂ into a neutralized amino acid salt solution and the heat of dissolution of formed solid in the solution. Provided experimental data could be used to improve the existing thermodynamic model and to provide a better estimate of energy requirement.

Nomenclature

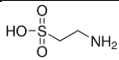
Am	Alkanolamine
FS	Full Scale
M	Molarity (mol/L)
MEA	Monoethanolamine
R	Reaction
SS	Stainless Steel
VLE	Vapour Liquid Equilibrium
H _{Abs}	Heat of Absorption
H _s	Heat of Dissolution
α	Loading (mol CO ₂ / mol Amine)

2. Experimental and Methods

2.1. Chemicals

The purchased chemicals were used as received without further purification. Aqueous solutions were prepared by dissolving the chemicals (Table 1) in the distilled de-ionized water until 1 L of final solution is obtained. The purity of KOH was taken into account during the solvent preparation and assuming the rest is water.

Table 1. List of chemicals.

Name	Structure	CAS No.	Supplier	Purity
Potassium Hydroxide	KOH	1310-58-3	Sigma Aldrich	90%
Taurine		107-35-7	Sigma Aldrich	99%

2.2. Experimental setup

A commercially available reaction calorimeter CPA 202 (ChemiSens AB, Sweden) used in this work is designed for operation at temperatures between -50°C and 200°C depending on the choice of a heating media and an external cooling system, and at pressures from vacuum to 20 bar. The reactor is submersed in the CPA202BU thermostat filled with a heating media.

A glass reactor with metal flanges and 2 different SS lids was used in this work. Distilled water was used as a heating media (limiting the experimental temperature to max 90°C), and tap water was used for an external cooling.

The glass reactor of $258.8 \pm 0.2 \text{ cm}^3$ total volume (Figure 1) is equipped with a manometer, Pt-100 temperature sensor (accuracy 0.1°C), SENSIT pressure gauge (1-10 bara, accuracy 0.15%FS), and a magnetic stirrer with maximum stirring up to 2000 rpm. CO_2 is fed to the reactor via a Bronkhorst Hightech mass flow controller (0.5 NL/min, accuracy 0.1% FS). All operation parameters (e.g. reactor temperature and pressure, CO_2 temperature and pressure, heat flow, CO_2 flow, etc.) are recorded as function of time using a ChemiCall software provided by Chemisens. Sensitivity of the calorimeter given by the producer is 0.1 Watt.

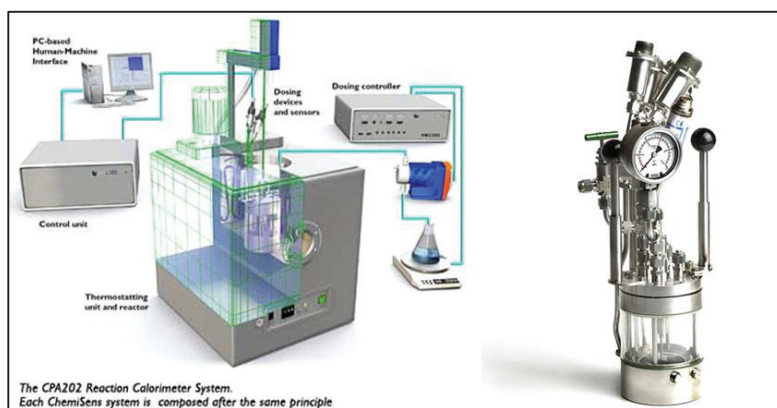


Figure 1. The CPA202 Reaction Calorimeter.

2.3. Experimental Procedures

Two different procedures to measure heat of absorption and heat of solid dissolution were used in this work. The procedure for the heat of absorption measurement similar to one described by Kim and Svendsen (2007) [7] was used in this work: the CO_2 was added in several steps to the solution kept at isothermal conditions. Amount of heat removed by the system to keep the solution at constant temperature was then assumed to be equal to the heat of absorption.

The reactor was filled with $\sim 150 \text{ g}$ solution and evacuated to $\sim 3 \text{ kPa}$ at ambient temperature. A desired experiment temperature was set and the system was left to reach equilibrium. The equilibrium was reached when reactor temperature, pressure and total power were constant for minimum 10 min. At this condition, approximately 0.02 mol

CO₂ was injected to the reactor. The existing equilibrium was disturbed during CO₂ addition therefore a waiting process to reach next equilibrium was required. When the next equilibrium was established, the next portion of CO₂ was added. Addition of CO₂ continued until the maximum set pressure in the reactor was reached (~400 kPa).

The experiment may be performed in an automatic mode, so the routines have been developed and verified by performing the measurements with 30mass % MEA solution. The routine for the heat of absorption measurements is provided in Figure 2a.

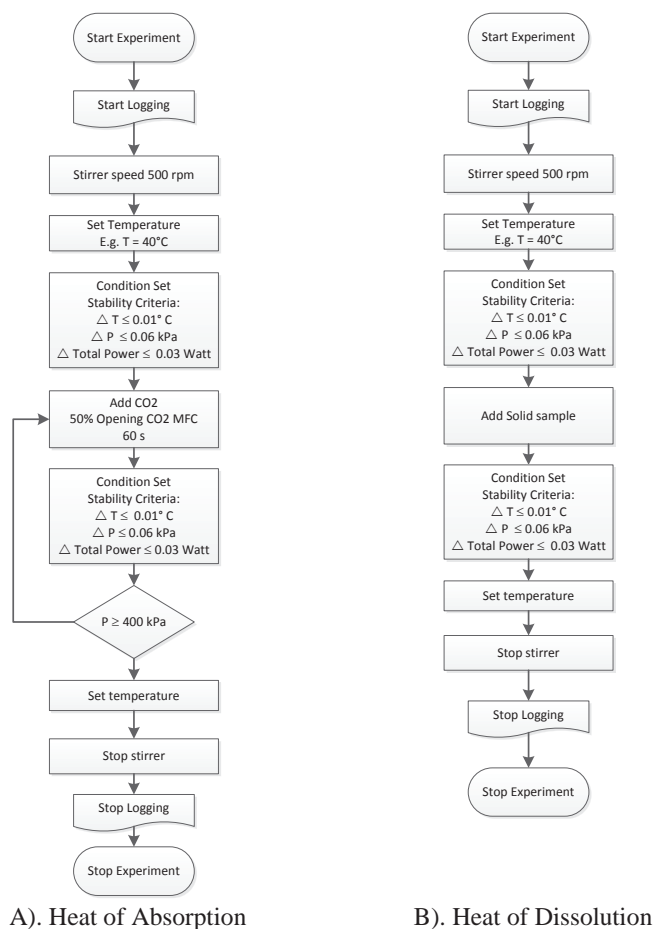


Figure 2. Developed experimental routines

For the heat of dissolution experiment, the glass reactor was connected with another SS-316 lid, equipped with a batch injector (sample holder) of the solids (~20 ml) (Figure 3). The reactor was filled with about 150 ml solution, while 1 to 5 grams solid sample was placed into the sample holder. The experiments were performed at constant temperature under ambient pressure (no evacuation).

The solid sample in the sample holder was weighted on a Mettler Toledo XP1203S balance (± 0.001 g). The sample holder was closed and screwed to the reactor lid protecting solid sample from any contact with the solvent. The reactor was then immersed into the thermostat unit.



Figure 3. Glass reactor with a lid equipped with the batch injector for the solids (www.chemisens.com)

A desired experiment temperature was set and system left to reach equilibrium. At equilibrium, the solids was dejected from the sample holder into liquid phase in the reactor and dissolved. The existing equilibrium was disturbed during solids addition therefore a waiting process was also required. When the new equilibrium is established then one experiment was done. The heat of dissolution experiment is a batch-wise experiment, since only one injection may be done. The routine for the heat of dissolution measurements is presented in Figure 2b.

3. Result and discussion

Procedures verification for the heat of absorption and the heat of dissolution measurements are presented below. Experimental data for the selected systems are tabulated in the Appendix A.

3.1. Verification of the experimental procedures

Verifications for both experimental procedures were done by running the experiments with known systems.

The heat of absorption procedure was verified using 30mass % MEA and the result shown in Figure 4. It may be seen that data from this work at both temperatures are about 7 % higher than the data reported by Kim, et al. [7]. The reason for this is not clear. The calorimeter is pre-calibrated by the producer. The reactor is equipped with an electrical validation heater (max 6 W) and a series of experiments with validation heater was run. The difference between the heat generated by the electric heater and heat measured in the calorimeter was within 4%. Data measured in this work are however agree well with the data from Lail et al [8] measured in the same type of calorimeter.

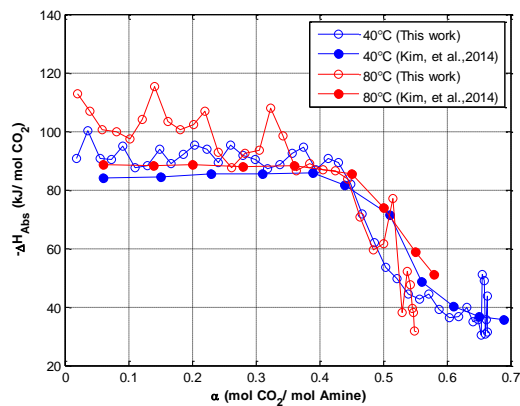


Figure 4. Heat of CO₂ absorption into 30mass % MEA solution at 40°C and 80°C: comparison with literature [9]

For the verification of the heat of dissolution procedure, experiments with Taurine dissolution in water, was performed at 40°C. The heat of dissolution is concentration dependent [10] and decreases as the amount of solids added increases for an exothermic reaction and vice versa. Therefore, the experiment has to be conducted at different concentrations. Thereafter, the heat of dissolution at infinite dilutions can be found by extrapolation (Figure 5).

Calorimetric study of the heat of dissolution of Taurine in water was reported at 25°C, i.e. 24.2 kJ/ mol [10] and 24.9 kJ/ mol [11]. The two reported values are about 3% different. No reported data was found at different temperatures, however Zittle and Schmidt [11] provided the correlation based on Van't Hoff equation to estimate the heat of dissolution at different temperatures and at infinite dilution. The heat of dissolution at 40°C was estimated to be 24.68 kJ/mol, which agrees well with the value estimated in this work.

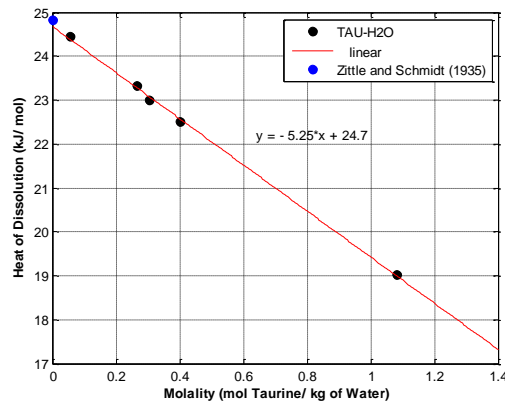


Figure 5. Heat of dissolution of Taurine in water at 40°C (Points - Experimental value; Line - linear correlation)

3.2. Heat of absorption of CO₂ in 1.5 M and 3.0M Potassium-Taurate (KTAU) solutions

Heat of absorption of 1.5 M KTAU was measured at 40°C and 80°C. Experiments were performed twice at each temperature to see the reproducibility. The results are presented in Figure 6. No solid formation was observed during the experiment as expected.

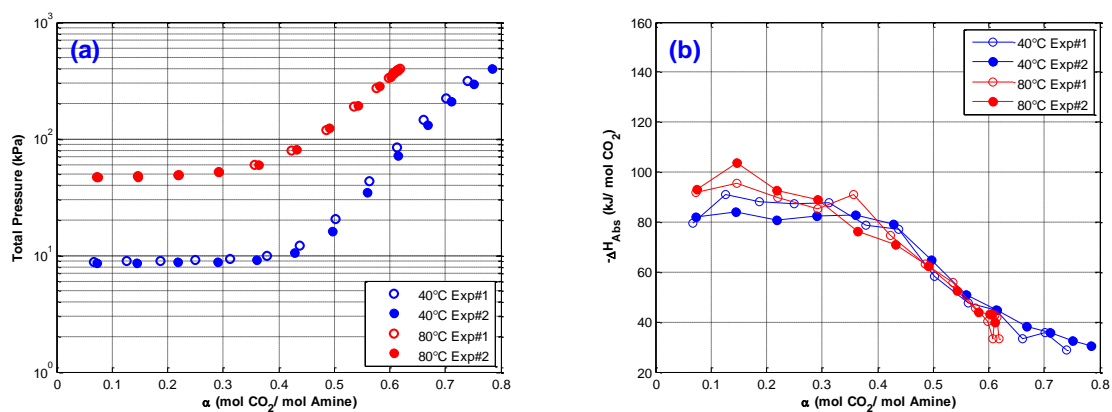


Figure 6. a) Pressure profiles and b) Heat of absorption of CO₂ in 1.5M KTAU solution as function of loading at 40°C and 80°C.

Heat of absorption of 3.0 M KTAU was measured at three temperatures:

- At 25°C, a sudden increase in the heat of absorption (about 20-30 kJ/mol-Amine) was observed at loading ~0.35-0.45 mol-CO₂/mol-Taurine due to a supersaturation. After this condition, more CO₂ uptake would cause the dissolved solute to precipitate. From there on, the heat of absorption is equal to heat of absorption and heat of crystallization (Figure 7b).
- At 40°C, the heat of absorption increased at loading ~0.5 mol-CO₂/mol-Taurine. The same reason for the experiment at 25°C could explain these phenomena.
- At 80°C, no solid formation was observed.

The solids formed during the experiment were collected and dried using a vacuum filter. The collected solids were used in the next experiments for heat of dissolution measurements.

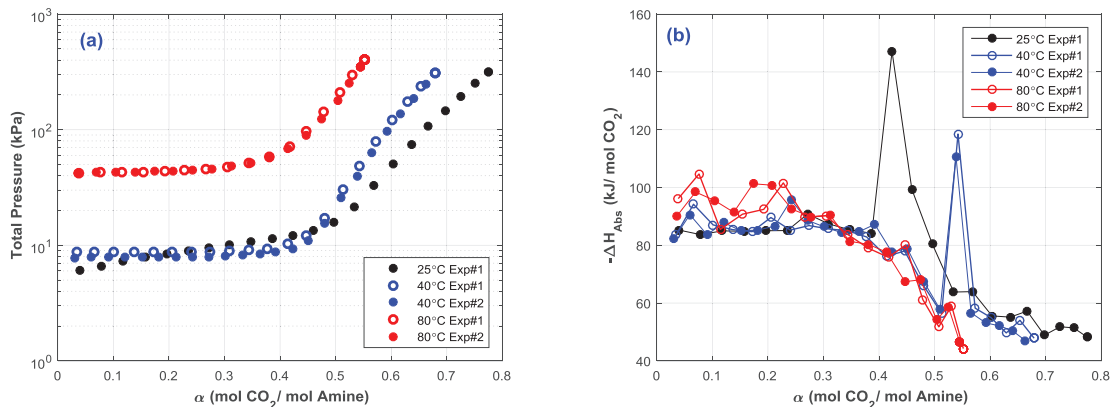


Figure 7a) Pressure profiles and b) Heat of absorption of CO₂ in 3.0M KTAU solution as function of loading at 25°C, 40°C and 80°C.

3.3. Heat of dissolution of the formed solids.

The heat of dissolution of the formed solids in water and in unloaded 3.0 M KTAU solution was measured at 40°C. The amount of solid sample varied between 1 and 5 grams. The experimental results are also collected in Table A1.6. (See Appendix A) and presented in Figure 8.

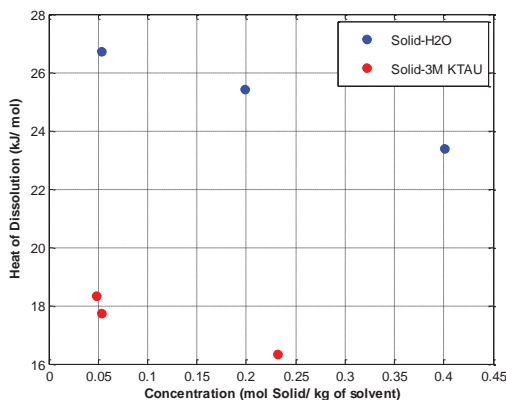


Figure 8. Heat of dissolution of solid in water and in 3.0 M KTAU and at 40°C

Experimental values for the heat of dissolution at infinite dilutions determined in this work by extrapolation are presented in Table 2.

Table 2. Heat of Dissolution for different systems at 40°C

System	Heat of Dissolution (kJ/mol Amine)
Taurine-H ₂ O	24.68
*Formed Solid-H ₂ O	27.27
*Formed Solid-KTAU 3.0M	18.52

*) Molecular Weight of Formed solid was assumed to be similar to that of Taurine

It may be seen from the results that the heat of dissolution of pure Taurine in H₂O is slightly lower than of the formed solids in water. This may be due to the presence of potassium bicarbonate in solid sample, which has high heat of dissolution [12]. In the experiment for the solids dissolution into KTAU 3.0M, the heat of dissolution was observed to be lower than in the two previous experiments.

4. Conclusion

Calorimetric study of Potassium-Taurate (KTAU)-CO₂ system was performed in a CPA202 calorimeter. Two different experiments were done, i.e. heat of absorption of CO₂ in KTAU solvent at different concentrations (1.5 M and 3.0 M), loadings (up to ~ 0.8 mol CO₂/ mol Taurine) and temperatures (25°C, 40°C and 80°C) and heat of dissolution of Taurine/ solid formed during the experiment in water or/and KTAU 3.0M at 40°C.

The developed procedure for measuring the heat of absorption was verified with MEA 30mass % at two temperatures (40°C and 80°C). The developed procedure for measuring the heat of dissolution was verified by measuring heat of dissolution of pure Taurine (solid) in water. The result agrees very well with the reported data.

The effect of solid formation was studied during the experiment of the heat of absorption of CO₂ into 3.0M KTAU at low temperatures (25°C and 40°C).

The heat of dissolution of the formed solid in water was slightly higher than that of Taurine in water. This may be due to the presence of potassium bicarbonate, which has higher heat of dissolution while the measured heat of dissolution for the formed solid into 3.0 M KTAU solution was slightly lower than the heat of dissolution of the same solids in water.

Acknowledgements

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Appendix A. Experimental Results

Table A1- 1. Heat of Absorption of CO₂ in 1.5M KTAU at 40 °C

Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂	Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂
0.07	8.83	79.56	0.07	8.60	81.91
0.13	8.91	90.84	0.15	8.67	84.18
0.19	8.96	88.09	0.22	8.69	80.81
0.25	9.04	87.32	0.29	8.82	82.46

0.31	9.25	87.64	0.36	9.15	82.67
0.38	9.83	78.93	0.43	10.47	79.07
0.44	12.12	76.98	0.50	16.12	64.98
0.50	20.66	58.33	0.56	34.48	51.01
0.56	42.85	47.67	0.62	72.22	44.97
0.61	84.88	44.97	0.67	130.48	38.38
0.66	145.42	33.35	0.71	206.95	35.94
0.70	222.49	35.87	0.75	297.50	32.59
0.74	315.24	28.67	0.78	399.37	30.56

Table A1- 2. Heat of Absorption of CO₂ in 1.5M KTAU at 80 °C

Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂	Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂
0.07	47.12	91.80	0.07	46.78	93.04
0.15	47.63	95.63	0.15	47.32	103.89
0.22	48.86	89.77	0.22	48.64	92.47
0.29	51.85	85.12	0.29	51.88	88.95
0.36	59.59	90.83	0.36	60.00	76.32
0.42	78.58	74.63	0.43	80.27	71.10
0.49	118.93	63.31	0.49	122.60	62.47
0.54	188.43	55.64	0.54	194.08	52.65
0.58	271.94	45.69	0.58	280.59	43.92
0.60	331.09	40.06	0.60	339.62	43.26
0.61	357.79	33.40	0.61	366.19	43.26
0.61	373.68	42.90	0.61	383.26	39.94
0.62	384.96	41.86	-	-	-
0.62	393.84	41.86	-	-	-
0.62	401.20	33.35	-	-	-

Table A1- 3. Heat of Absorption of CO₂ in 3.0M KTAU at 25 °C

Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂	Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂
0.04	7.58	85.83	0.04	6.07	85.30
0.08	9.36	86.26	0.08	6.64	83.69
0.12	11.57	91.42	0.12	7.22	84.99
0.16	13.31	89.92	0.16	7.86	84.85
0.20	15.44	85.83	0.20	8.44	85.03
0.24	17.08	86.36	0.24	9.02	85.11
0.28	19.11	92.63	0.27	9.48	90.83
0.32	21.12	88.04	0.31	10.09	87.38
0.36	23.09	87.90	0.35	10.69	85.33

0.40	25.39	137.71	0.39	11.34	84.14
0.43	27.52	95.26	0.42	12.23	147.10
0.47	30.46	83.06	0.46	13.31	99.38
0.51	36.13	76.01	0.50	15.72	80.37
0.56	47.41	58.85	0.53	21.56	63.82
0.58	65.01	57.62	0.57	33.02	63.96
0.62	89.30	53.75	0.60	50.56	55.56
0.65	120.94	50.19	0.64	74.93	55.14
0.68	160.40	45.63	0.67	106.66	57.23
0.71	207.77	49.83	0.70	146.38	48.87
0.74	262.99	42.22	0.73	194.57	51.80
0.77	323.13	49.78	0.75	251.34	51.42
-	-	-	0.77	316.57	48.20

Table A1- 4. Heat of Absorption of CO₂ in 3.0M KTAU at 40 °C

Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂	Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ Habs) kJ/mol CO ₂
0.03	8.75	83.70	0.03	7.82	82.38
0.07	8.77	94.20	0.06	7.85	90.58
0.10	8.76	87.06	0.09	7.89	83.68
0.14	8.83	85.41	0.12	7.90	87.85
0.17	8.83	84.71	0.15	7.90	85.02
0.21	8.81	89.62	0.18	7.90	85.26
0.24	8.83	85.27	0.21	7.97	86.60
0.27	8.78	86.83	0.24	7.98	95.69
0.31	8.90	85.68	0.27	7.98	88.61
0.34	9.04	85.05	0.30	8.11	86.37
0.38	9.37	82.88	0.33	8.22	84.31
0.41	10.38	76.17	0.36	8.33	84.68
0.45	12.12	78.01	0.39	8.68	87.24
0.48	17.19	66.13	0.42	9.38	77.73
0.51	30.46	56.44	0.45	11.06	78.82
0.54	48.33	118.51	0.48	15.41	67.34
0.57	79.36	58.25	0.51	25.56	57.77
0.60	121.55	54.96	0.54	39.44	110.80
0.63	173.38	49.66	0.57	63.42	56.63
0.65	236.56	54.04	0.59	96.23	53.12
0.68	307.57	47.84	0.62	137.56	52.12
-	-	-	0.64	187.86	50.36
-	-	-	0.66	246.12	47.06

Table A1- 5. Heat of Absorption of CO₂ in 3.0M KTAU at 80 °C

Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ H _{abs}) kJ/mol CO ₂	Loading (α) mol-CO ₂ /mol-Am	P kPa	(- Δ H _{abs}) kJ/mol CO ₂
0.04	42.35	96.16	0.04	42.49	90.07
0.08	42.55	104.68	0.07	42.62	98.43
0.11	42.78	85.49	0.10	42.90	95.52
0.15	43.06	90.76	0.14	43.14	91.41
0.19	43.54	92.43	0.17	43.49	101.29
0.23	44.37	101.59	0.21	44.00	100.79
0.27	45.43	89.66	0.24	44.82	92.51
0.30	47.48	90.20	0.28	46.00	89.89
0.34	51.21	83.84	0.31	48.04	90.44
0.38	58.10	79.02	0.35	51.49	81.38
0.42	71.87	75.85	0.38	57.60	80.33
0.45	97.68	80.09	0.41	69.04	77.61
0.48	142.96	61.19	0.45	89.87	67.41
0.51	209.32	51.79	0.47	125.02	68.06
0.53	298.07	59.01	0.50	179.79	54.17
0.55	403.16	44.25	0.52	255.13	58.74
-	-	-	0.55	349.04	46.50

Table A1- 6. Heat of Dissolution of Taurine/ Formed solid in pure water/ 3.0M KTAU at 40 °C

System	m (mol/ kg)	(Δ Hs) (kJ/ mol)	System	m (mol/ kg)	(Δ Hs) (kJ/ mol)	System	m (mol/ kg)	(Δ Hs) (kJ/ mol)
TAU-H ₂ O	0.0557	24.44	Solid-H ₂ O	0.0532	26.72	Solid-3M KTAU	0.0478	18.35
	0.2663	23.33		0.1983	25.41		0.0533	17.74
	0.3064	22.99		0.4005	23.37		0.2315	16.35
	0.4006	22.52		-	-		-	-
	1.0820	19.02		-	-		-	-

References

- [1] R.J. Hook, An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds, *Ind. Eng. Chem. Res.*, 36 (1997) 1779-1790.
- [2] P.S. Kumar, J.A. Hogendoorn, G.F. Versteeg, P.H.M. Feron, Kinetics of the reaction of CO₂ with aqueous potassium salt of taurine and glycine, *AIChE Journal*, 49 (2003) 203-213.
- [3] A.F. Portugal, P.W.J. Derks, G.F. Versteeg, F.D. Magalhães, A. Mendes, Characterization of potassium glycinate for carbon dioxide absorption purposes, *Chemical Engineering Science*, 62 (2007) 6534-6547.
- [4] E.S. Hamborg, J.P.M. Niederer, G.F. Versteeg, *J. Chem. Eng. Data*, 52 (2007) 2491.
- [5] E.S. Fernandez, E.L.V. Goetheer, DECAB: Process development of a phase change absorption process, *Energy Procedia*, 4 (2011) 868-875.
- [6] E. Sanchez Fernandez, K. Heffernan, L.V. van der Ham, M.J.G. Linders, E. Eggink, F.N.H. Schrama, D.W.F. Brilman, E.L.V. Goetheer, T.J.H. Vlught, Conceptual Design of a Novel CO₂ Capture Process Based on Precipitating Amino Acid Solvents, *Industrial & Engineering Chemistry Research*, 52 (2013) 12223-12235.
- [7] I. Kim, H.F. Svendsen, Heat of Absorption of Carbon Dioxide (CO₂) in Monoethanolamine (MEA) and 2-(Aminoethyl)ethanolamine (AEEA) Solutions, *Industrial & Engineering Chemistry Research*, 46 (2007) 5803-5809.
- [8] M. Lail, J. Tanthana, L. Coleman, Non-Aqueous Solvent (NAS) CO₂ Capture Process, *Energy Procedia*, 63 (2014) 580-594.
- [9] I. Kim, K.A. Hoff, T. Mejdell, Heat of Absorption of CO₂ with Aqueous Solutions of MEA: New Experimental Data, *Energy Procedia*, 63 (2014) 1446-1455.
- [10] H.P. Hopkins, C.-H. Wu, L.G. Hepler, Thermochemistry of Aqueous Aminosulfonic Acids. Sulfamic and Sulfanilic Acids and Taurine, *The Journal of Physical Chemistry*, 69 (1965) 2244-2248.
- [11] C.A. Zittle, C.L.A. Schmidt, Heats of solution, heat of dilution and specific heats of aqueous solutions of certain Amino Acids, *Journal of Biological Chemistry*, 108 (1935) 161-185.
- [12] S.J. Vevelstad, Kim, I., Grimstvedt, A., Wiig, M., and Aronu, U. E., Study of degradation and heat of dissolution of solids in aqueous blend of AMP and KSAR loaded with CO₂, in: 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland, 2016.