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PHASE EQUILIBRIUM MEASUREMENTS OF AMMONIA BASED CO_2 CAPTURE SOLVENTS WITH FTIR FOR GAS PHASE ANALYSIS

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Abstract

Vapor-liquid-solid equilibrium (VLSE) was measured for four solvents (blends A-D) at atmospheric pressure in a low-temperature setup at 20 ºC and at 20, 35, and 55 ºC for blend E. The blends are ammonia-based aqueous solutions selected to evaluate the potential for CO_2 capture at post-combustion conditions with high pressure solvent regeneration. The set-up was modified to enable analysis of ammonia and CO_2 in the vapor phase using FTIR®. Solid formation in the liquid phase was monitored using optical probes FBRM® and PVM® to determine maximum CO_2 loadings for the precipitation-free range.

Keywords: *vapor-liquid equilibrium, solvent, carbon dioxide, ammonia*

1. Introduction

Solvent technology for CO_2 capture has been demonstrated at different scales and several processes are now commercially available from a few suppliers. However, to mitigate climate changes, more cost-effective technologies and technology provider are necessary. Research on the development of more energy efficient and low-cost solutions is ongoing in many different projects around the world. Water-lean solvents and solvents allowing to strip the CO_2 at higher pressure are considered promising as having potential to reduce CO_2 capture cost significantly. Cost reduction potential for CO_2 capture due to lower heat capacity and high reaction kinetics are reported for some non-aqueous solvents [1], while the solvents that can be regenerated at higher pressure allow savings in the cost (both OPEX and CAPEX) of CO_2 compression.

Several solvent formulations were tested in the present work to evaluate their performance in terms of CO_2 solubility and absorption capacity and explore a potential for high pressure stripping. Ammonia-based solvents for CO_2 capture have several advantages compared to monoethanolamine (MEA) which is often used as a reference solvent [2]-[3]. The main advantages are low cost, no degradation and potential for high-pressure high-temperature stripping. The main disadvantages of this type of solvents are very high volatility of the ammonia and operational challenges due to formation of solid ammonia bicarbonate from vapor phase on cold surfaces.

Only a few work report measurements of the ammonia in the vapor phase over aqueous ammonia solutions using gas chromatography (GC), see for example [4]-[6]. No experimental data are found for ammonia-based mixtures.

In the CLIMIT Demo project IMPRESS (2019-2021) candidate solvents were evaluated for high-pressure stripping applications aiming at the demonstration of the best performing candidate at SINTEF's Tiller CO2Lab, which will be equipped with a high-pressure stripper in 2021 in the MPSolv project funded through the ECCSEL ERIC program.

In the IMPRESS project absorption performance was evaluated for several solvent blends containing 5 mole ammonia per kg water (molal concentration) mixed with an amine and potassium carbonate, or only with amines. The objective was to evaluate the effect of solvent composition on ammonia volatility and absorption capacity for CO_2, and to estimate potential for high pressure stripping for a blend with the most promising absorption performance.

Absorption performance (phase equilibrium) was measured at 20 ºC in a low-pressure set-up with in-situ analysis of the gas phase. Potential for high pressure stripping was assessed by extrapolating the low temperature data to a higher temperature using an inhouse empirical model [7]. Additionally, Aspen Plus simulation was also utilized in this performance assessment.

2. Experimental

2.1. Chemicals

Chemicals were used as received without additional purification. Aqueous solutions were prepare using distilled de-ionized water. All solvent blends consisted of 5 mole ammonia (NH_3) per kg water, 0 or 2 mole K_2CO_3, and 2-2.5 mole amine according Table 1.

Table 1. IMPRESS blends tested in this work

Coded name	Composition, molal basis		
	NH_3	K_2CO_3	Amine
Blend A	5	2	2 amine A
Blend B	5	2	2 amine B
Blend C	5	2	2 amine C
Blend D	5	0	2 amine D
Blend E	5	0	2 amine A + 0.5 amine D

2.2. Experimental set-up and procedure

Partial pressure of CO_2 and NH_3 over loaded solutions at absorber conditions was measured using the LabMax® (Mettler Toledo) reactor setup connected to an analytical instrument for the analysis of the vapor in the head space.

The setup consists of a mechanically agitated jacketed glass reactor of 1 L volume, equipped with Pt100 temperature sensor (uncertainty 0.1 ºC), Leo3 pressure transducer (0-30 bar, uncertainty 0.1 % FS), and probes for online Particle Vision and Measurement (PVM) and Focused Beam Reflectance Measurement (FBRM) for characterization of phase change systems (liquid-liquid or liquid-solid).

For the head space analysis in the present study, the setup was connected to the ABB Fourier Transform infrared spectroscopy (FTIR) gas analyzer via a heated transfer line. The vapor phase is circulated using an inline micropump (RS PRO Diaphragm Electric Operated Positive Displacement Pump). To avoid condensation/ precipitation of the ammonium salts, the reactor lid and tubing are heat traced and kept at the same temperature as the reactor. Vapor sample is transferred to the FTIR via a transfer line kept at 180ºC, same temperature as in the FTIR cell. Any degradation of amines due to high temperature was assumed negligible due to short residence time at high temperature and relatively short experimental time. Liquid samples (5-7 ml) are taken at each equilibrium point and analyzed for CO_2 (Apollo 9000 Combustion TOC Analyzer) and total alkalinity (acid-base titration).

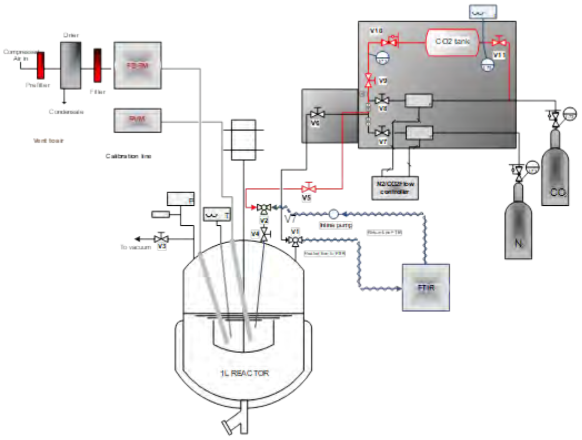

Figure 1**:** Experimental setup for VLSE measurements with FTIR for head space analysis, and PVM and FBRM for solid phase monitoring.

The experiments were terminated when precipitation took place. Precipitate formation was monitored using FBRM and PVM optical probes.

Precipitation-free operation was selected as one of the criteria for solvent optimization. To determine the saturation loading, at which no more CO_2 is solvable in the liquid phase, the experiment was stopped when precipitation was observed. At this point, the stirrer was stopped to allow the precipitate to settle (Figure 2) and a liquid sample of clear liquid without precipitate was taken. An example of the precipitate images taken with PVM is shown in Figure 3. No analysis of the precipitate was done, however, based on the earlier work, we can say from the crystals shape that the solids are most probably potassium bicarbonate crystals.

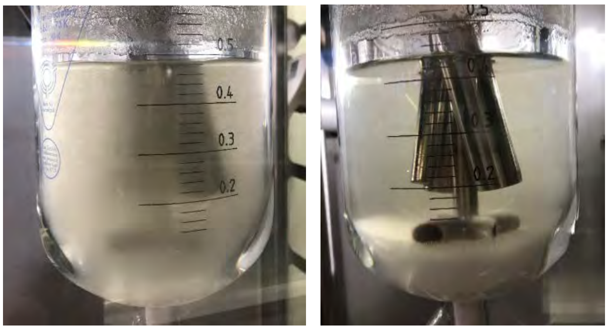

Figure 2: Images of the reactor with solvent (522 DPD) at the last loading point when precipitation took place (above, left), and after precipitate was left to settle (above, right).

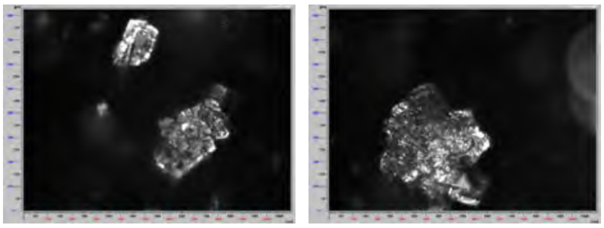

Figure 3: Images of the formed crystals taken with PVM®.

2.3 Calibration of FTIR

The FTIR was used for the analysis of CO_2 and NH_3 in the gas phase. The instrument was calibrated with the premixed calibration gases, supplied by a gas provider together with the certificate of analysis. Calibration for CO_2 was done using 1000 ppm, 2.5, 5, 10, and 40 vol% CO_2 in nitrogen. Calibration for ammonia was done using 1, 5, and 15 vol% ammonia in nitrogen.

The premixed gases were used to acquire calibration spectra, which in turn were used for the development of component models. The FTIR model performance vs calibration gas composition is shown in Table 1.

Table 2: FTIR model performance vs. calibration gas

	FTIR (vol %)	**Calibration Gas (vol %)**	**Absolute relative deviation (%)**
CO_2 (vol%)	0.09	0.10	7.72
	2.53	2.50	1.32
	4.94	5.00	1.24
	9.32	10.00	6.84
	14.29	15.00	4.72
	39.76	40.00	0.59
NH_3 (vol%)	1.08	1.00	8.04
	5.29	5.00	5.74
	15.92	15.00	6.10

As maybe seen from Table 2, there is a room for improvement of the FTIR models, i.e., more calibration data points are needed to tweak the component models. This will be done in future work.

2.4 Validation of the experimental procedure

For the validation of the experimental procedure for measuring partial pressure of CO_2 using FTIR, VLE measurements with 30 wt% MEA solution was done and data compared with literature data [8]. Partial pressure of CO_2 measured in this work using FTIR agrees well with the data reported by Aronu et al. [8] (see Figure 4). A major advantage is that FTIR allows analysis of the ammonia in the vapor phase in addition to CO_2.

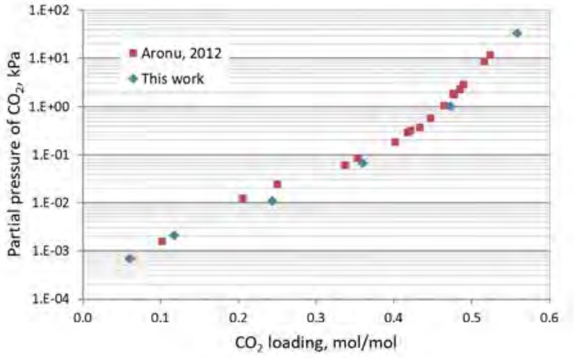

Figure 4: Partial pressure of CO_2 over 30 wt% MEA solution at 40°C as function of CO_2 loading: comparison with literature data.

To validate ammonia pressure measurements, partial pressure of ammonia for Blend A is compared with predictions from AspenPlus. As seen in Figure 5bthe measured results agree very well with the simulation results.

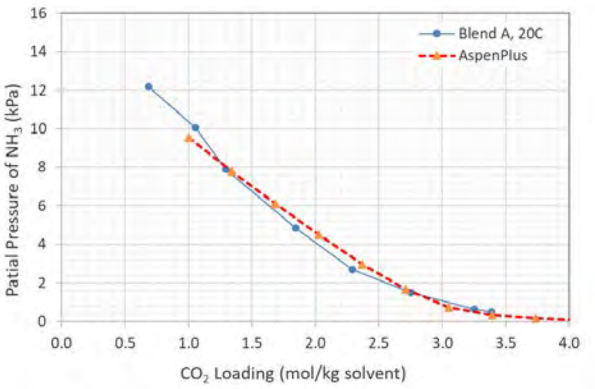

Figure 5. Equilibrium partial pressure of ammonia for Blend A measured at 20 °C using FTIR compared with AspenPlus predictions.

3. Results and Discussion

Experimental partial pressure of CO_2 in the gas phase tested at 20 °C is compared with data for 30 wt% MEA at 40 °C (reference solvent at its optimal absorption temperature) as shown in Figure 6a. Lower partial pressure of CO_2 after CO_2 loading of about 2.5 mol/kg for all blends presently studied indicates that all of them have higher CO_2 absorption capacity. Partial pressure of ammonia in the gas phase above the same blends at 20°C is compared as shown in Figure 6b. It should be noted that CO_2 loading in these plots includes CO_2 introduced to the solvent with K_2CO_3. (1 mol/kg). As may be seen from the figure, partial pressure of ammonia above the blend E is the lowest. This solvent was therefore selected for further testing to evaluate its potential for high pressure stripping.

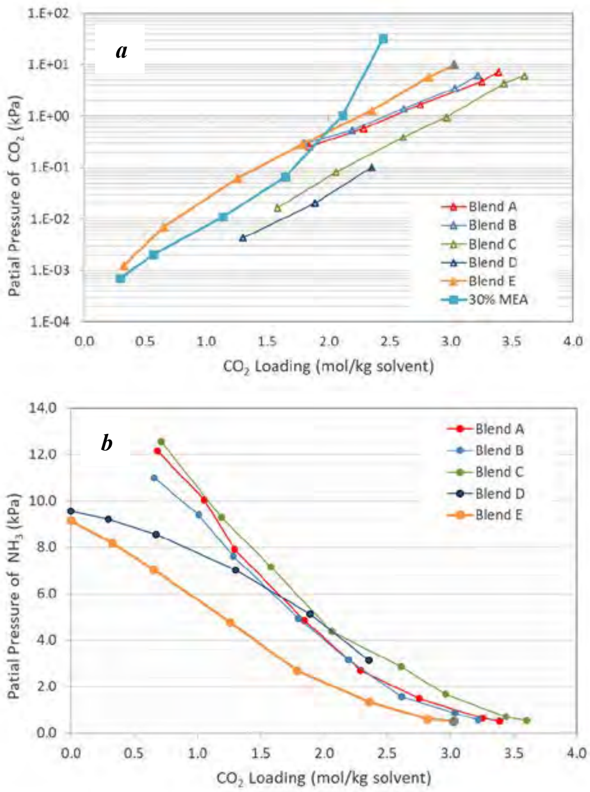

Figure 6. Experimental partial pressure of CO_2 (a) and NH_3 (b) for tested solvent blends at 20 °C.

Equilibrium partial pressure of CO_2 and ammonia for the blend E was also measured at 35 and 55 °C. Tests at higher temperature is not possible in the same setup using the same procedure because total pressure is higher than atmospheric. To compensate for the lack of experimental data at stripper conditions (120 °C), the experimental data for this solvent blend measured at 20, 35 and 55 °C, were used to develop a vapor-liquid equilibrium (VLE) model for predicting equilibrium at 120 °C, thus allowing assessment of the cyclic capacity and potential for high pressure stripping with this solvent. The model is based on the assumption of constant heat of absorption for a specific loading. This assumption is embedded in the derivation of the Gibbs Helmholtz equation (see [7] for further details). This assumption on constant heat of absorption is reasonable for data with moderate span in temperatures and has been applied to a lot of solvent systems studied by SINTEF. This is seen, also from experimental data, as an almost equal distance between VLE isotherms when plotted on logarithmic or semilogarithmic scale. Thus, it is believed that the extrapolation to 120 ºC is reasonable for the present study, but obviously this should be validated at a later stage.

The model fit for the P_{CO2} data is shown in Figure 7*a* also including the VLE curve for 120 ºC predicted by the model. Experimental and modelled partial pressure of NH_3 for the same blend is shown in Figure 7*b*.

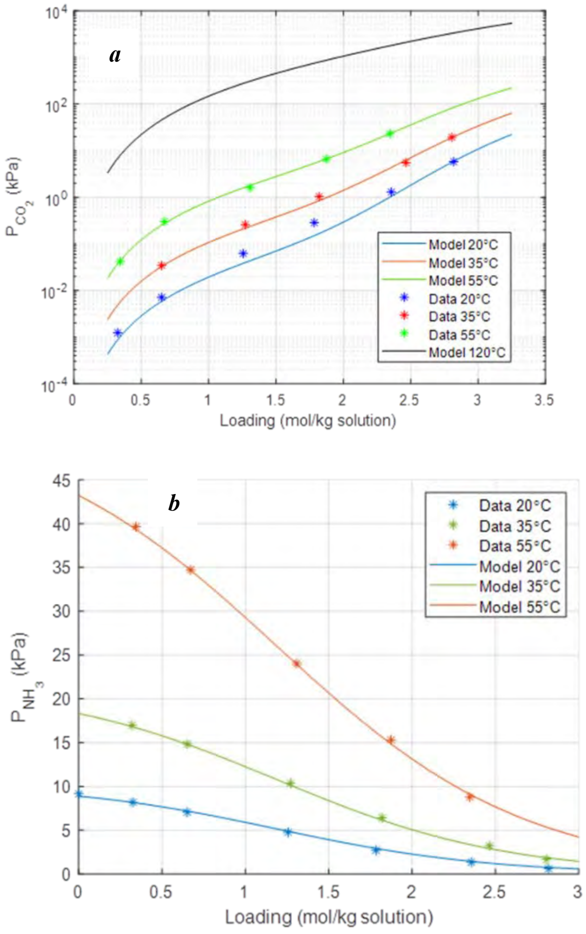

Figure 7. Partial pressure of CO_2 (a) and NH_3 (b) for the blend E at 20, 35, and 55 ºC: experimental and modelling results.

To estimate partial pressure of ammonia for this blend at stripper conditions 120ºC, extrapolation was also done.

Results for solvent blend E at 20 and 120 ºC compared with data for 30 wt% MEA at 40 and 120 ºC, shown that blend E has much higher absorption capacity and higher partial pressure of CO_2 at stripper conditions. The improved capacity is clearly shown in Figure 8 as the distance between the equilibrium isotherms at absorber conditions (40 ºC) and stripper conditions (120 ºC) for both solvents systems.

Furthermore, total pressure in the stripper will be very high due to ammonia vapor pressure making it possible to strip the CO_2 at higher pressure.

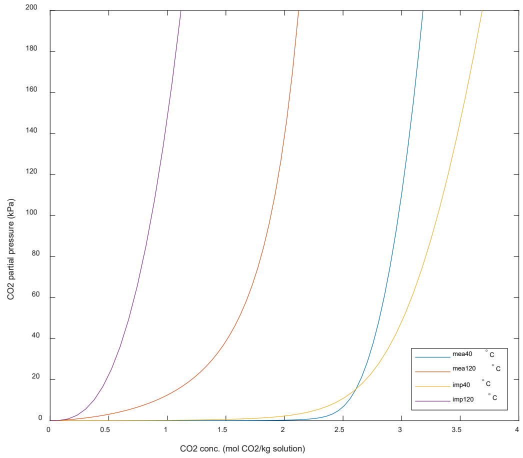

Figure 8: CO_2 equilibrium based on an equilibrium model for 30 wt% MEA at 40 and 120 ºC compared to the solvent E (imp in the figure) in the present study.

4. Conclusions

A low-pressure set-up available at SINTEF was connected to FTIR to enable measurements of both CO_2 and ammonia in the vapor phase and VLE for the selected solvent blends measured at 20 ºC. The experimental procedure was validated and good agreement with literature data or with simulations in AspenPlus was observed.

One of the tested blends was selected for further characterization to evaluate the potential for high pressure stripping and testing at Tiller CO2Lab.

Even though it was concluded that stripping will be possible at high pressure (7-10 bar), some considerations are necessary before this solvent can be tested in the Tiller pilot.

During VLE measurements it was observed that even though the reaction rate is high in the beginning, it is decreased quickly, and considerable time is needed to reach the equilibrium at higher CO_2 loadings. This means that higher residence time may be needed for this solvent in the absorption column, or a higher column may be needed.

Partial pressure of ammonia is still very high at the absorber conditions requires implementation of a system to capture and return ammonia to the process, as well as preventing emissions. The existing water configurations at Tiller CO2Lab are very efficient with amines but will not be sufficient with an NH_3-rich solvent. The acid wash system will capture emissions but will imply a loss of NH_3 that should be returned to the process.

At stripper conditions, operational challenges are foreseen due to possibility of solids formation from vapor phase on the cold surfaces. For testing at pilot scale, the stripper section of the pilot has to be carefully heat traced to avoid any cold spots. This seems to be challenging in the condenser, where water and ammonia should be separated from CO_2 leaving the desorber column. A solution for this issue needs to be prepared and implemented at Tiller before this solvent can be tested.

Acknowledgements

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