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Promoted strong bicarbonate forming solvents for CO$_2$ Capture

Ardi Hartono[a]*, Solrun J. Vevelstad[b], Inna Kim[b], Rune Rennemo[a] and Hanna K. Knuutila[a]

[a]Norwegian University of Science and Technology (NTNU), Sem Sælands vei 4, Trondheim NO-7491, Norway
[b]Sintef Materials and Chemistry, Sluppen PO BOX, Trondheim, Norway

Abstract

Effect of different promoters on performance of two bicarbonate forming solvents (HS1 and HS2) was studied in this work and results compared with the performance of 30 wt% MEA and CESAR1 solvents. Based on the results from rapid screening experiments (absorption at 40ºC, desorption at 80ºC), one promoter was selected for further study. Vapor-liquid equilibrium (VLE) and heat of absorption were measured for two solvent systems promoted with the selected promoter.

Keywords: Promoters, Strong Bicarbonate, Screening, VLE, Absorption Heat.

1. Introduction

Better solvent candidates for CO$_2$ capture technology should have high net cyclic capacity, fast reaction/absorption rates for CO$_2$, low heat of reaction, high chemical stability, low vapor pressure and low corrosiveness [1]. Different types of amines have been used such as alkanolamines and polyamines. Alkanolamines react with CO$_2$ to form either carbamate or bicarbonate [1]:

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* Corresponding author. Tel.: +47-735 50 338; fax: +47-735 84 080.
  E-mail address: ardi.hartono@ntnu.no

$$CO_{2(\ell)} + 2Am \leftrightarrow AmCO_2^- + AmH^+ \qquad\qquad (R_1)$$

$$CO_{2(\ell)} + H_2O + Am \leftrightarrow HCO_3^- + AmH^+$$

(R_2)

Primary and secondary amines undergo both carbamate and bicarbonate formation (reactions R_1 and R_2) while tertiary amines only form bicarbonate (R_2). The bicarbonate-carbamate ratio is an important parameter when selecting systems with potentially high cyclic capacity and reasonable good absorption rate [2].

In our previous works [3], different strong bicarbonate forming solvents were tested in the screening apparatus and their absorption (40°C) and desorption (80°C) performance (rate of absorption/desorption, rich and lean loadings) compared. Rapid screening experiments also provide information on solvent behavior, such as foaming, solidification, phase change, color change, etc. The difference between the rich and the lean loadings gives an indication of the cyclic capacity of solvent. In the previous work two promising solvent candidates, with much higher cyclic capacity than 30 wt% MEA, were identified. However, the rate of absorption is much lower than that of MEA, hence a promoter/activator to enhance absorption rate is needed.

Different promoters have been tested in literature, e.g. enzymes [4, 5], inorganic (e.g. arsenic trioxide, alkali metal salts of selenious) [1] and organic compounds [6]. A blend of alkanolamines/ amines could be one of the alternatives. In this work, different alkanolamines were used as promoters for both solvents. Performance of the blends were tested in the same setup as described in previous work [3]. The results are compared to the data for 30 wt.% MEA and CESAR1 [7, 8] solvents. Based on the screening experiments and also taking into account environmental properties of the promoters, one promoter was selected for further study. VLE and heat of absorption for the promoted solvent systems were measured and the results are used for the estimation of energy consumption for regeneration of solvents [9].
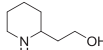

Nomenclature

Am	Amine
FS	Full Scale
MEA	Monoethanolamine
R	Reaction
R_{CO_2}	Reaction rate (mol/kg/s; mol/kg/h)
SS	Stainless Steel
VLE	Vapor Liquid Equilibrium
H_{Abs}	Heat of Absorption (kJ/mol)
α	Loading (mol CO2/ mol Amine)

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2. Experimental setups and procedures

2.1. Chemicals

The commercially available chemicals are purchased from Sigma Aldrich. The chemicals, listed in Table 1, were used without further purification. All solutions containing promoters are prepared gravimetrically.

Table 1. List of chemicals.

NO.	Chemical Name	Abbreviation	CAS No.	Structure	Purity (%min)	Comment
1	2-Piperidineethanol	2-PPE	1484-84-0		95	HS1
2	1-(2-Hydroxyethyl)pyrrolidine	1-(2HE)PRLD	2955-88-6		97	HS2
3	Promoters	P1 to P7	-		97	
4	Carbon Dioxide	CO2	124-38-9	CO_2	99.999	
5	Nitrogen	N2	7727-37-9	N_2	99.998	

2.2. Screening Apparatus

The screening apparatus mimics an absorption (40°C and 95% CO_2 captured) and desorption (80°C and 90% CO_2 removal) processes in CO_2 capture plant and thus allows comparison of performance (rich/ lean loading and cyclic capacity) of different solvents to that of a reference solvent. [6, 10-13] .

The set-up (Figure 1) consists of a jacketed glass reactor (~150 cm³) equipped with a sintered gas sparger and magnetic stirrer. Temperature in the reactor is measured using a thermocouple (Pt100, ±0.1°C) and controlled using a LAUDA E5 heating bath with water as a heating medium. Bronkhors® High-Tech mass flow controllers (MFC) for N_2 and CO_2 are used to adjust the feed gas compositions (maximum flow of 1NL/min). All gas leaving the reactor was sent to a Fisher–Rosemount BINOS® 100 NDIR CO_2 analyzer.

About ~0.125 kg solvent was introduced into the reactor and heated to set temperature (40 °C). When the absorption temperature was reached, a CO_2/N_2 gas mixture was bubbled through the solution in the reactor. The initial CO_2 inlet concentration was kept constant at 10% CO_2 (10 kPa partial pressure) during absorption process at 40°C which was stopped at 95 % absorption when the CO_2 outlet concentration showed 9.5 % .

For desorption process, the CO_2 rich solution was heated to 80°C. During this period, it is commonly seen that some CO_2 has already escaped from the solution and when reached at 80°C, a constant mass flow of N_2 (0.9 NL/min) was used as a swipe-gas to remove CO_2 from the solution. The desorption was ended when the CO_2 partial pressure in the outlet gas reached 1 kPa.
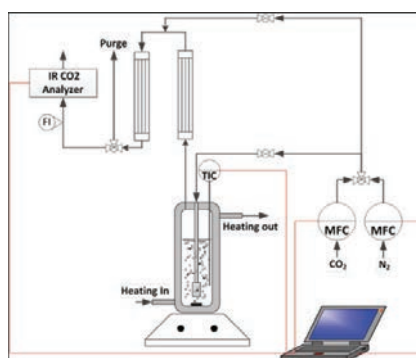

Figure 1. Screening set-up (MCF, Mass Flow Controller; TIC, Temperature Indicator and Control; FI, Flow indicator; IR CO2, Infra-red Carbon Dioxide)

2.3. Equilibrium Apparatuses

Vapor liquid equilibrium was measured using two setups: the atmospheric pressure VLE apparatus (40°C), shown in Figure 2a, and medium pressure VLE apparatus (80 and 120°C), shown in Figure 2b. The partial pressure of CO_2 was measured in the first apparatus using IR CO_2 analyzer, while in the second apparatus it was estimated from the total pressure, assuming a constant vapor pressure of solvent during an isothermal experiment. More details on the experimental procedures may be found in our previous work [14].
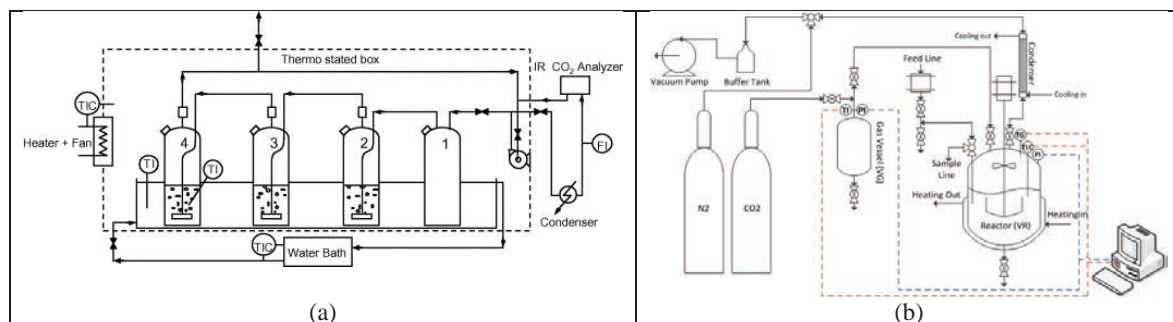

Figure 2. Atmospheric pressure (a) and medium pressure (b) VLE apparatuses

2.4. Calorimeter

A CPA202 reaction calorimeter (Figure 3) was used for measuring the heat of absorption in this work. The calorimeter is designed for operation at temperatures between -50°C and 170°C depending on the choice of a heating media and an external cooling system, and at pressures from vacuum to 20 (glass reactor) or 100 (SS reactor) bars. The reactor is submersed in the CPA202BU thermostat filled with a heating media.

The calorimeter is a glass reactor with metal flanges and a SS lid. Distilled water was used as a heating media (limiting the experimental temperature to max 90 °C), and tap water was used for the external cooling.

The reactor is equipped with a Pt-100 temperature sensor (accuracy 0.1°C), SENSIT pressure gauge (1-10 bara, accuracy 0.15%FS), and a propeller stirrer. CO_2 is fed to the reactor via a mass flow controller (0.5 NL/min, Bronkhorst® Hightech). 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 W.

The experimental procedure used in this work is similar to one used by Kim, et al. [15]. The detail procedure can be found in Hartono, et al. [16]. About 120 g of the solution was used in each experiment. The CO_2 was added batch-wise to the solution kept at isothermal conditions.
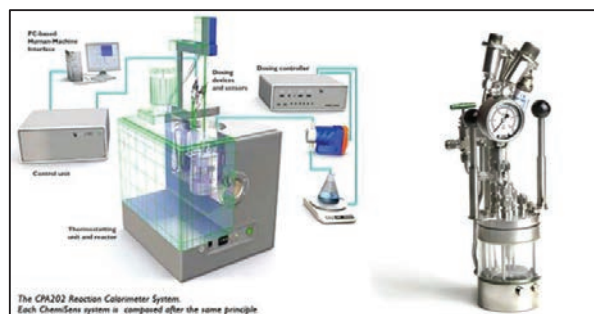

Figure 3. The CPA202 Reaction Calorimeter.

3. Result and discussion

Six promoters were tested in this work. Solutions with constant concentration ratio of promoters to solvents (HS1 and HS2) were prepared and tested in the screening apparatus.

Figure 4 shows the absorption and desorption curves from the screening experiments for the promoted HS1 solvents together with the original (un-promoted) HS1, 30 wt% MEA, and CESAR1. It may be seen from the Figure 4(a) that the initial absorption rate of the promoted solvents is not significantly improved in the presence of the promoters since the original HS1 solvent (without promoter) has already high initial absorption rate. However, absorption capacity of the promoted solvents is higher than that of the original solvent. Solvent promoted with P6 and P7 show faster initial absorption rate than MEA and CESAR1 solvents and also increased loading capacity (rich loading). Solvent promoted with P1 and P5 show a similar rich loading to CESAR 1 and slightly better than that of MEA.
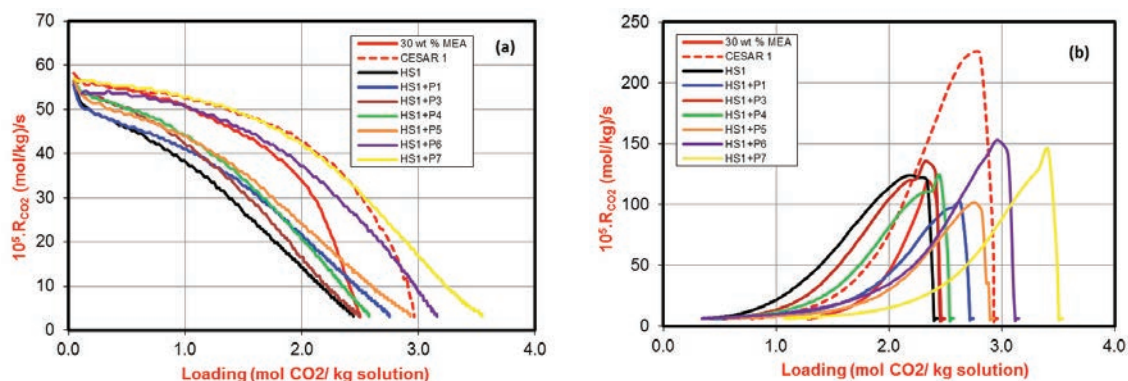

Figure 4. Absorption (a) and desorption (b) rates of the HS1 solvent at 40°C and 80°C, respectively.

The desorption curves is presented in the Figure 4(b). It may be seen that the promoters P3, P4, P6 and P7 enhance the desorption. However, CESAR 1 solvent remains the fastest one to desorb CO_2 from solution.

The screening performance of the promoted HS1 solvents are compared in Figure 5. It may be seen from the figure that the initial absorption rate remains similar (~2.0 mol CO_2/kg solution/h) for all tested blends. The HS1, promoted with P3 and P4 absorbed less CO_2 than MEA. Solvent promoted with P1, P3 and P5 absorbed CO_2 similar to MEA, while solvents promoted with P6 and P7 absorbed more CO_2 than that of MEA and CESAR 1 solvents. The desorption rate was not improved by promoters but the solvent promoted with P6 show the leanest loading. Only promoters P6 and P7 showed a better cyclic capacity compared to the HS1 solvent without promoters.
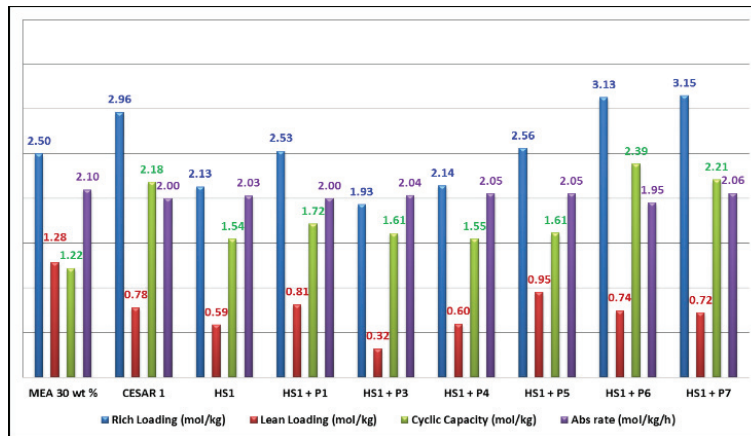
Figure 5. Solvent performances of the Promoted HS1 together with MEA 30 wt. % and CESAR1 solvents

Figure 6 shows the absorption and desorption curves from the screening experiments for the promoted HS2 solvents together with the original solvent. It may be seen from the Figure 6(a) that promoters enhance significantly the initial absorption rates of the HS2 solvent. With P6 and P7 promoters, the initial absorption rate is similar to MEA and CESAR1 solvents, also higher rich loading were observed for both systems. Solvent promoted with P1, P3, P4 and P5 enhance the initial absorption rate of the HS2 solvent however the rate is slower than that of MEA and CESAR1 solvents. Solvent promoted with P1 and P5 show rich loading similar to MEA.
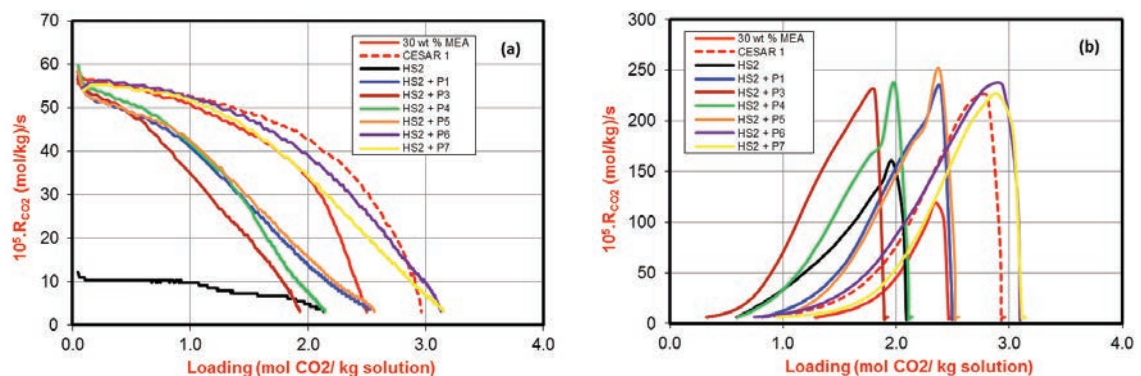

Figure 6. Absorption (a) and desorption rates (b) of the HS#2 solvent at 40°C and 80°C, respectively.

Desorption performance is presented in the Figure 6(b). It may be seen that all promoters enhance the desorption rate. Furthermore more CO_2 is released, and leaner loadings than that of 30 wt% MEA were observed.

An overview of the screening performance of the promoted HS2 solvents systems is given in Figure 7. The initial absorption rate increased significantly from 0.44 to ~2.0 mol-CO_2/kg-solution/h with all tested promoters. The rich loadings of the original HS2, and solvents promoted with P1, P3 and P4 are similar to MEA. The promoter P5 has rich loading similar to CESAR1. Systems promoted with P6 and P7 have absorption capacities higher than CESAR1. The solvent promoted with P6 show the leanest loading. Similar to the results for the HS1 solvent, only promoters P6 and P7 improve cyclic capacity of the original solvent.
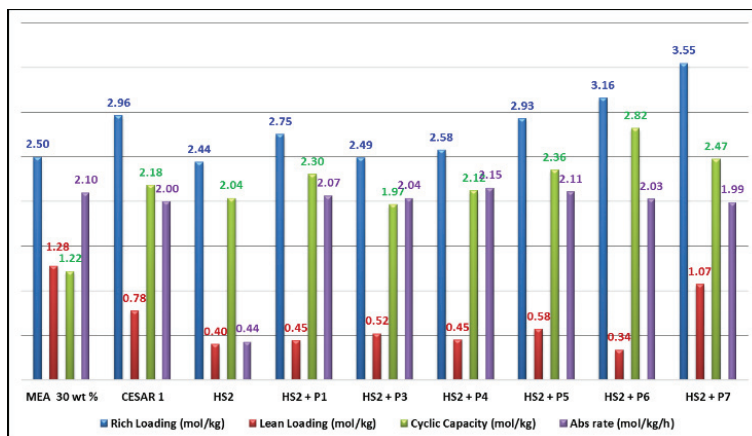
Figure 7. Solvent performances of the Promoted HS2 together with MEA 30 wt. % and CESAR1 solvents

The screening results showed that solvents promoted with P6 and P7 had better performance than MEA and CESAR1 solvents. However, one of the promoters is classified as toxic by the supplier, while the other one may have environmental issues due to its degradation products. Further study is necessary if one of these promoters will be used. Therefore in this work, the promoters P4 was selected for further testing for VLE and heat of absorption measurements.

The VLE experiments at 40°C were conducted in a low-pressure apparatus (see Figure 2a), while at 80°C and 120°C a medium pressure apparatus was used (see Figure 2b). The measured VLE data were fitted to an empirical correlation [6, 14], a soft VLE model, which was further used for energy estimation for solvent regeneration [9]. The experimental results and model predictions are showed in the Figure 8a (promoted HS1 solvent) and Figure 8b (promoted HS2 solvent). The reported VLE model [14] for non-promoted solvents are also included for comparison of the CO_2 solubility in these solvents. It may be seen from the figures, the slope of the curves with the promoter has changed as expected. While the change is not very significant for the HS1 (Figure 8a), the curves for the HS2 are more "vertical" (see Figure 8b) indicating that that higher capture rate maybe expected and the pinch in the absorber avoided.
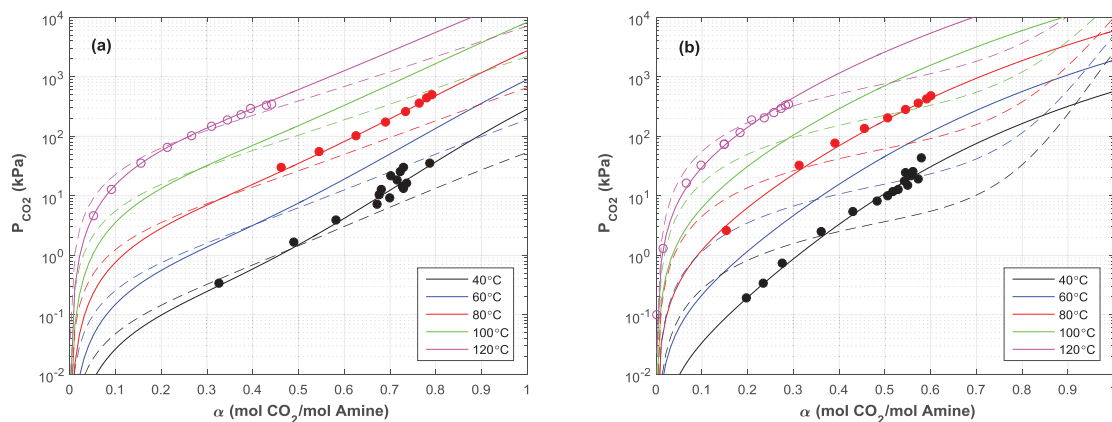

Figure 8. Equilibrium models at different temperatures (40°C, 60°C, 80°C, 100°C and 120°C) for (a) HSA1 (b) HSA2 solvents (Solid lines, promoted systems; Dashed lines, Non-promoted systems).

Heat of absorption of the promoted solvents measured in this work are compared to the results for 30 wt% MEA measured the same set-up in Figure 9. It may be seen from the figure, that heat of absorption of the promoted systems highly depends on loading and is in general lower than that of 30 wt% MEA.
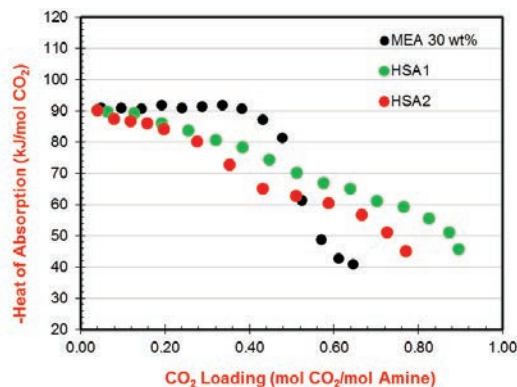

Figure 9. Heat of absorption of CO2 for activated solvents (HSA1 and HSA2) compared with that for 30 wt% MEA solution at 40 °C

4. Conclusion

Screening apparatus was used to test different promoters for HS1 and HS2 solvents [3]. The absorption (at 40°C) and desorption (80°C) curves as function of loading are presented and discussed. Based on the screening results and taking into account environmental issues, one promoted was selected for further tests.

For the promoted solvent systems (HSA1 and HSA2), the VLE was measured at 40°C, 80°C and 120°C and a soft model developed. Heat of absorption of CO_2 was measured at 40ºC.

Better absorption rate, higher cyclic capacity and lower heat of absorption of new promoted systems is expected to improve the solvent performance and reduce the energy consumption compared to 30 wt% MEA and CESAR1.

Acknowledgements

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