

## Structure-Property Relationships for New Amines for Reactive CO<sub>2</sub> Absorption

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New amines for reactive absorption of CO<sub>2</sub> from synthesis gas were developed, synthesized, and characterized. All studied amines are derivatives of triacetone amine (TAA) and differ only in the substituent of the basic TAA ring structure. In a first step, a short list of candidates was established. Selected candidates were then synthesized and studied experimentally. Gas solubility, rate of absorption, liquid-liquid and solid-liquid equilibrium, viscosity, and chemical equilibria were studied. Based on the knowledge gained in the evaluation of the results, new candidates were proposed. In the iterative process, about 50 amines were considered and 27 of them were actually synthesized and investigated. All synthesized amines were assessed on the same data basis. From the 27 synthesized amines the eight most promising for industrial applications were evaluated with the newly developed NoVa short-cut method. This method yields estimates for the energy demand. The well-established solvent MDEA/PZ (Piperazin-activated Methyldiethanolamine) was included in the study. Four candidates show an improved performance compared to MDEA/PZ, with energy savings up to 30 %. The large body of results was also used to establish relationships between the chemical structure of the amines and their properties as reactive solvents for CO<sub>2</sub> capture. NMR data on the chemical reactions in the studied systems and data from titration curves was used for that purpose. The influence of differences in the chemical structure of the amines on the different properties was elucidated and related to the performance of the solvents for CO<sub>2</sub> capture.

### 1. Introduction

The development of new amines for CO<sub>2</sub> absorption for post combustion carbon capture has received much attention in the last years (Singh et al. (2007), Puxty et al. (2009), Notz et al. (2011), Ermatchkov et al. (2011), Wagner et al. (2013), Vasiliu et al. (2016), Behrens et al. (2017)). But CO<sub>2</sub> absorption is also important in many established large-scale industrial processes, like the purification of synthesis gas and natural gas. Reactive absorption/desorption is widely used in these processes for CO<sub>2</sub> removal. However, the energy demand for that separation is high and it is interesting to develop new solvents with superior properties also for such applications. Therefore, in the present project novel amines for the removal of CO<sub>2</sub> from synthesis gas by reactive absorption were developed and tested. The work was realized in a co-operation between Evonik Industries, thyssenkrupp, and the Laboratory of Engineering Thermodynamics (LTD) of University of Kaiserslautern.

All studied amines are derivatives of triacetone amine (TAA) (see Fig. 1). These amines have not been considered before as reactive solvents for CO<sub>2</sub> capture. The TAA derivatives are named Evonik Amines (EVA) here. The approach of the present work is characterized by a shake-hand between the knowledge-guided synthesis of the new TAA-based amines and their characterization as solvents. A schema of the workflow is shown in Figure 1. In a first step, a short list of TAA-based amines that looked promising was established and the possibilities to synthesize them were evaluated. These amines differ only in the substituent of the basic TAA ring structure, see Figure 1. Some of the candidates were then synthesized and studied experimentally in a screening. The measurements include: solubility and rate of absorption of CO<sub>2</sub>, liquid-liquid and solid-liquid

equilibrium and viscosity. Furthermore, basic physico-chemical data like acid constants, and chemical equilibrium constants, namely those of the carbamate formation, were determined. The same procedures were applied for all amines. The results were used to establish relationships between the chemical structure of the amines and their properties as reactive solvents for CO<sub>2</sub> capture. Based on these relationships, new candidates were identified, added to the list and tested as described previously. In this iterative process, about 50 amines were considered and 27 of them were actually synthesized and investigated.

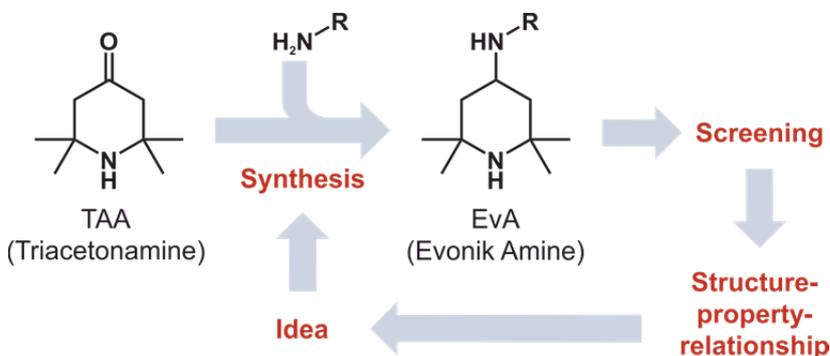


Figure 1: Project work flow for the shake-hand approach between knowledge-guided synthesis of the new Evonik Amines and their characterization as solvents.

## 2. Experimental Procedure

### 2.1 EvA Synthesis

The EvAs are synthesized via reductive amination and purified by vacuum distillation and filtration. The purity of the amines is determined by gas chromatography and NMR spectroscopy and is > 0.95 g/g for most EvAs studied here. The most important impurities are educt rests and water. Also oxidation and degradation products of the educts and the product were observed. 12 of the studied EvAs are solid and 15 are liquid as pure components at ambient conditions.

### 2.2 Experimental Setup and Procedure

The experimental set-ups and procedures used in the present work were recently described in detail by Vasiliu et al. (2016). As a standard, solutions with 0.4 g/g EvA in water were used for the tests. Both CO<sub>2</sub>-loaded and unloaded solutions were studied and the same procedures were applied for all EvAs.

Solid-liquid equilibria were measured in unloaded and CO<sub>2</sub>-loaded solutions. The solubility of CO<sub>2</sub> in the aqueous EvA solution was measured by head-space gas chromatography at pressures below 1.5 bar. Absorption kinetics and foaming were studied in a flow saturator, which also yielded preliminary results for the gas solubility. Acidity constants were determined by titration and the speciation of the solutions was investigated by <sup>13</sup>C inverse gate decoupled NMR spectroscopy. For chemical structure elucidation also 2D NMR experiments were carried out.

## 3. Results and Discussion

### 3.1 Assessment for industrial application

Five of the 27 synthesized EvAs are not sufficiently soluble in water. Another 14 show solid precipitation when the aqueous solution is loaded with CO<sub>2</sub>. For these reasons, 19 EvAs were discarded so that only 8 remained which were studied more comprehensively. For these the gas solubility was determined at 40 °C and 100 °C. The results are shown in Figure 1 a) together with results from their correlation. For that correlation, a new equation was used which is called SolISOFT, see Vasiliu et al. (2016). EvA03, EvA34 and EvA36 show very high CO<sub>2</sub> loadings at 40 °C but also higher loadings than the other amines at 100 °C. The largest difference between the isotherms at 40 °C and 100 °C is found for EvA03.

The correlations of the gas solubility data were used for assessing the solvents. A new short-cut method was used for that purpose that was developed in the present project. It is called NoVa (see Vasiliu et al. (2016)) and is an improved version of the method of Notz et al. (2011). The method yields estimates for the specific energy demand and recirculation rate for a given CO<sub>2</sub> removal task. Figure 1 b) shows results that were obtained with the NoVa method for the five most promising EvAs. The task was to lower the partial pressure of CO<sub>2</sub> in a syngas from 2 bar to 0.5 mbar. The results were calculated for isothermal operation of the absorber

(40 °C) and desorber (100 °C). In Figure 1 b) the specific energy demand is plotted as a function of the liquid to gas mass flow ratio in the absorber. As strong assumptions are used in the NoVa short-cut method the absolute numbers shown should not be over-interpreted, but experience shows that the method yields useful rankings of solvents. For comparison also results from a well-established solvent are included in Figure 1: it is a solution of Piperazine (0.05 g/g) activated Methyldiethanolamine (0.35 g/g) in water and called MDEA/PZ here. The results for MDEA/PZ shown in Figure 1 were obtained based on the data from Ermatchkov et al. (2011) in the same way as those for the EvAs. A reduction of the energy demand of up to 30% for EvA03 compared to MDEA/PZ is found.

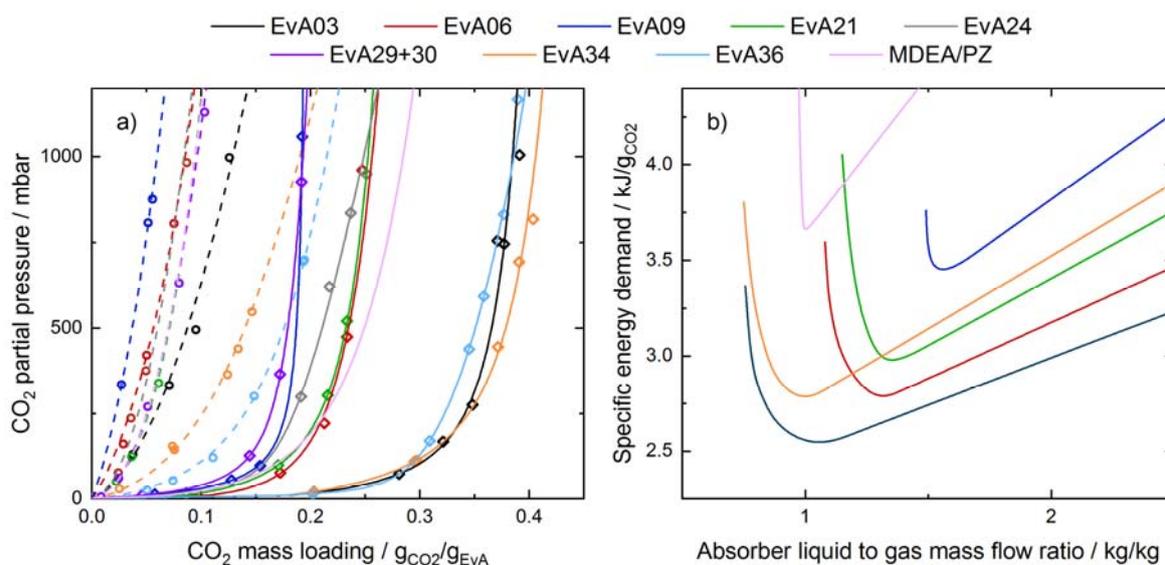


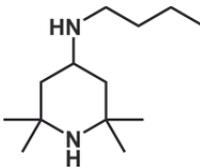
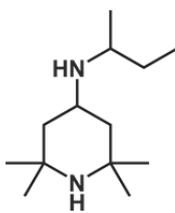
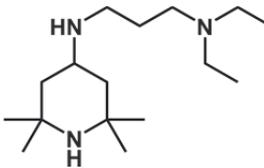
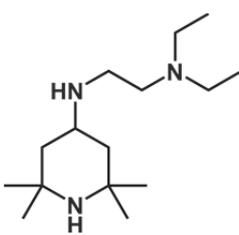
Figure 1: a) Absorption isotherms for 40 °C (diamonds, solid lines) and 100 °C (circles, dashed lines). The symbols are experimental data from the present work, the lines results from the SolSOFT equation. b) Specific energy demand as a function of the liquid to gas mass flow ratio in the absorber for a typical syngas purification task obtained with the NoVa short-cut method.

### 3.2 Structure property relationships

In Figure 2 a) results from flow saturator experiments are shown which were carried out with different aqueous amine solutions at 40 °C and a partial pressure of CO<sub>2</sub> of 140 mbar. In those experiments, the amine concentration in the solvent was 0.05 g/g so that also poorly soluble amines could be studied. The initial CO<sub>2</sub> absorption rate is plotted over the equilibrium loading of CO<sub>2</sub>. The EvAs are divided into two groups: those which contain oxygen and those which do not. As reference, also results for Monoethanolamine (MEA) and Piperazine activated Methyldiethanolamine (mass ratio: 1 / 7) (MDEA/PZ) are shown that were obtained in the present work with the same apparatus. The dashed line is the result of a linear fit to the entire data set. A general trend of increasing absorption rate with increasing loading is observed. This result is not surprising as the absorption is driven by the concentration gradient. Assuming that this influence is represented by the linear fit, the deviations of the results of the different amines from the fit represent differences in the kinetics that do not stem from differences in the loading. They may result from differences in the reaction kinetics, but can also result from physical effects that influence the kinetics, like the bubble size, which depends on the viscosity.

EvA 01 and MEA show the highest absorption rate. These two amines are the only ones in the study with a primary amino group, which probably explains the fast reaction kinetics. All other amines contain only secondary or secondary and tertiary amino groups. But also for these amines significant differences in the CO<sub>2</sub> loading and absorption rate are observed. In general, the oxygen-free EvAs show higher CO<sub>2</sub> loadings and higher absorption rates than the EvAs that contain oxygen. This is a result of two negative effects: on the one hand, oxygen atoms increase the molar mass of the EvA without capturing significant amounts of CO<sub>2</sub>. On the other hand, the oxygen atoms attract electrons and thus lower the basicity of the nitrogen atoms.

Table 1: Chemical structures, molar mass, acidity constants, and BM numbers for four EvAs.

Chemical structure										
Label	EvA02		EvA05		EvA25			EvA26		
Molar mass	212.4		212.4		269.4			255.4		
$pK_a$	10.3	7.9	10.3	7.8	10.3	9.3	6.4	10.1	8.9	4.5
BM	0.086		0.085		0.097			0.092		

To merge and describe both effects a novel characteristic number, the basicity per mass (BM) is introduced. The BM is calculated by dividing the sum of the measured  $pK_a$  values from titration experiments by the molar mass of the amine. Figure 2 b) shows the  $CO_2$  loading as a function of the BM. Besides data for 40 °C that were already shown in Figure 2 a), also results obtained in the same apparatus at 100 °C are shown in the diagram. A lower BM leads to lower  $CO_2$  loadings. The same holds for the absorption rate and the cyclic capacity (difference between the  $CO_2$  loadings at 40 °C and 100 °C) as Figure 2 c) and d) shows. All EvAs that contain no oxygen show higher BM than the ones that contain oxygen. With only a few exceptions the EvAs without oxygen perform better than those with. As examples, four of the studied EvAs that do not contain oxygen are shown in Table 1.

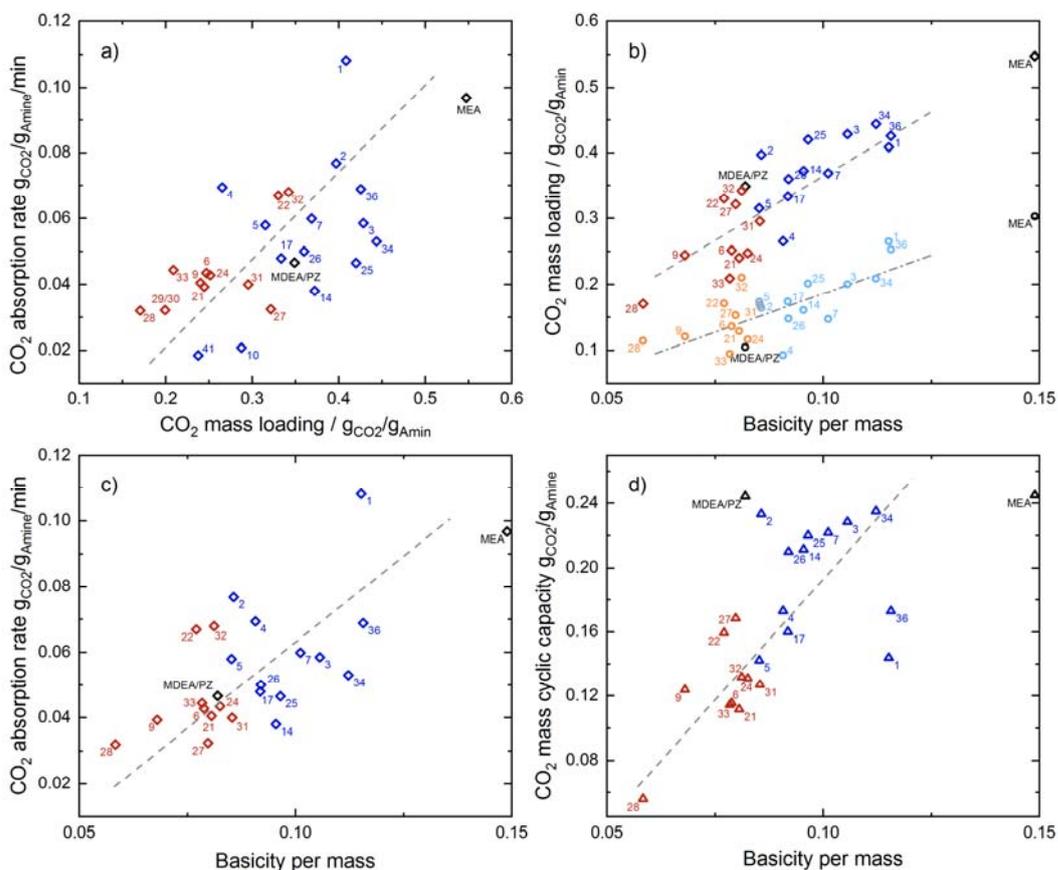


Figure 2: a)  $CO_2$  absorption rate over the  $CO_2$  loading. b)  $CO_2$  loading, c)  $CO_2$  absorption rate and d)  $CO_2$  cyclic capacities as a function of the basicity per mass BM (see text), respectively.  $CO_2$  absorption rate and  $CO_2$  loadings are obtained from flow saturator experiments at 40 °C (diamonds), 100 °C (circles) and between 100 and 40 °C (triangles).

The BM number describes essentially only the basicity of the amine. But for the performance of the amine also chemical reactions of the amine with  $\text{CO}_2$  are relevant. They were studied with NMR spectroscopy. In the following, results for the four EvAs shown in Table 1 are discussed. Figure 3 shows the results for fraction of amines that is present as carbamate as a function of the  $\text{CO}_2$  loading for aqueous solutions of the four EvAs with  $x_{\text{EvA}} = 0.1$  g/g at  $20^\circ\text{C}$ . The difference between the overall  $\text{CO}_2$  loading and the carbamate loading is  $\text{CO}_2$  captured as carbonate/bicarbonate and very low amounts of elementary dissolved  $\text{CO}_2$ . The corresponding carbamate structures are also shown in Figure 3.

EvA25 and EvA26 form significant amounts of carbamate. Up to 50 % of the available EvA is present as carbamate. Contrarily, only little carbamate is formed in EvA02 and EvA05. The carbamate formation is obviously strongly enhanced by the presence of the second amino group in the TAA substituent. This is explained here as a consequence of the formation of a stabilizing ring structure, cf. Figure 4. Upon dissolution of the amine in water, a partial protonation of the nitrogen atoms occurs ( $\text{R}_1$ ), the solution becomes basic and (bi)carbonate is formed ( $\text{R}_{\text{II}}$ ). Furthermore,  $\text{CO}_2$  forms a carbamate with secondary amine group of the substituent ( $\text{R}_{\text{III}}$  and  $\text{R}_{\text{IV}}$ ). The carbamate is stabilized by a delocalized proton, and is represented in Figure 4 as a Zwitterion. Reactions  $\text{R}_1$  to  $\text{R}_{\text{IV}}$  are possible in all four EvAs discussed here. For EvA25 and EvA26 an additional reaction ( $\text{R}_{\text{V}}$ ) is postulated here: In that reaction, the protonated tertiary nitrogen atom coordinates with the negatively loaded oxygen of the carbamate to form an internal salt with a ring structure, cf. Figure 4. The formation of the internal salt and the ring closure favor the carbamate stability. There are six atoms in the ring for EvA26 and seven for EvA25. Six-membered rings are usually more stable than seven-membered rings. This is in line with the finding that the carbamate formation is favored in EvA26 compared to EvA25.

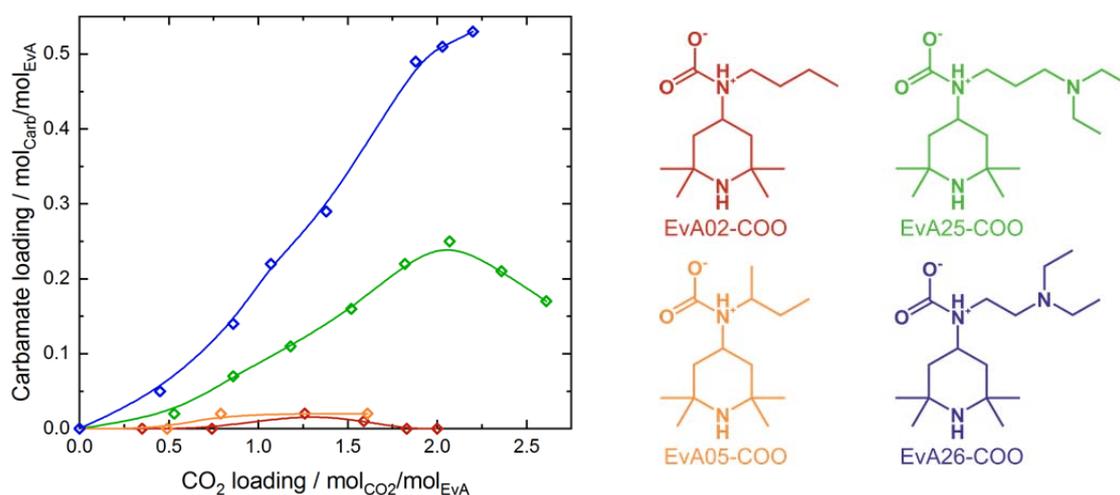


Figure 3: Left: Carbamate loading as a function of the overall  $\text{CO}_2$  loading from  $^{13}\text{C}$  inverse gated NMR experiments of aqueous EvA solutions with  $x_{\text{EvA}} = 0.1$  g/g at  $20^\circ\text{C}$ . Symbols show the experimental results, lines give a guide to the eye. Red: EvA02, orange: EvA05, green: EvA25 and blue: EvA26. Right: Chemical structure of the carbamate species elucidated by  $^{13}\text{C}$ - $^1\text{H}$  2D NMR spectroscopy.

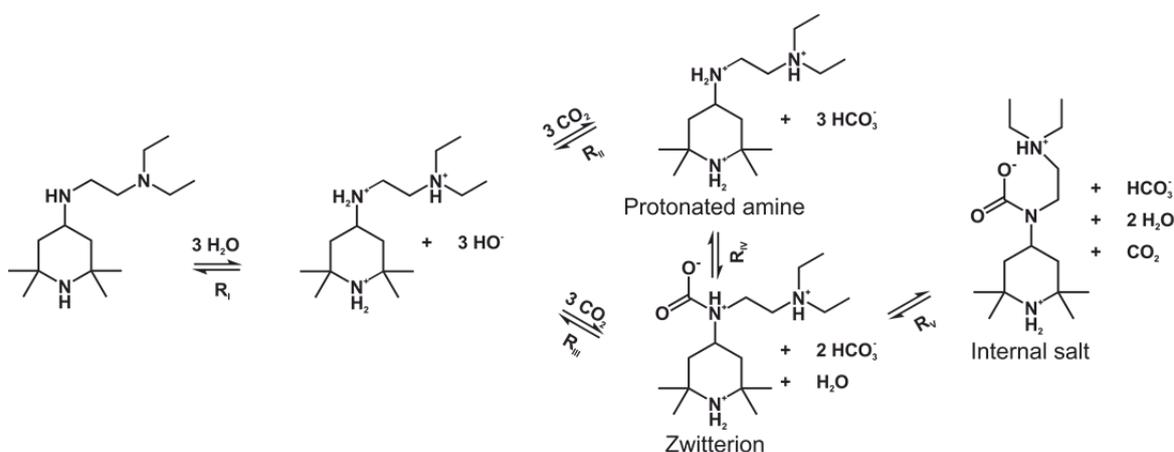


Figure 4: Chemical reactions in  $\text{CO}_2$  loaded aqueous solutions of EvA26.

#### 4. Conclusions

A shake-hand approach between the knowledge-guided synthesis of the new amines and their characterization as solvents was realized in a co-operation project between academic and industrial partners. A new class of amines for CO<sub>2</sub> capture is introduced: the TAA-based EvAs. Twenty-seven EvAs were synthesized and studied systematically. A new short-cut method for assessing solvents for CO<sub>2</sub> capture was developed and applied to the EvAs as well as to standard solvents, revealing superior properties of some of the EvAs. Furthermore, the comprehensive data-base was used to develop qualitative and quantitative structure-property relationships for the EvAs that enhance the understanding of the amine behavior and their performance in the CO<sub>2</sub> capture process.

#### References

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