Physico-chemical properties of the system N,N-dimethyl-dipropylene-diamino-triacetonediamine (EvA34), water, and carbon dioxide for reactive absorption

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Abstract

Aqueous solutions of N,N-dimethyl-dipropylene-diamino-triacetonediamine (EvA34) are promising solvents for CO₂ capture. Therefore, in the present work, a comprehensive experimental study was carried out to determine data on physico-chemical properties of EvA34 and its mixtures with H₂O and CO₂. The liquid density and the dynamic viscosity was studied for pure EvA34, as well as for unloaded and CO₂-loaded

aqueous solutions of EvA34. The liquid heat capacity was studied for pure EvA34 and unloaded aqueous solutions of EvA34. Furthermore, data on the vapor pressure of pure EvA34 was recorded. The pH-value was measured for unloaded and CO₂-loaded aqueous solutions of EvA34 and the dissociation constants of EvA34 were determined from titration curves. Moreover, data on the solubility of CO₂ in aqueous solutions of EvA34 and data on the CO₂-containing species in the liquid phase of these solutions were recorded. Most of the new data was taken at temperatures between 293 and 393 K. The mass fraction of EvA34 in the unloaded aqueous solutions was either $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g or $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. The CO₂-loading was up to $\tilde{\alpha}_{\text{CO}_2} = 6.2$ mol/mol. The new data were compared to corresponding data of two standard amines that are used for CO₂ capture: monoethanolamine (MEA) and a blend of methyl-diethanolamine and piperazine (MDEA/PZ). The comparison revealed that EvA34 combines favorable properties of MEA and MDEA/PZ in one molecule.

Introduction

The removal of CO₂ from gaseous streams is an important task in many industries. Natural gas and synthesis gas purification are among the largest applications in which CO₂ has to be removed from gaseous streams.^{1,2} This task is usually accomplished by reactive absorption.³ High requirement has to be met in the absorption process, e.g. the concentration of CO₂ in the purified gas must often be decreased to a few ppm.⁴ Common solvents that are used in this process are aqueous solutions of amines, of which many have been described in the scientific and patent literature.^{5,6} The solvent is regenerated by desorption. A drawback of the reactive absorption/desorption process is the high energy demand for the regeneration of the solvent. There have been many efforts to find new solvents with superior performance in the process, e.g. with lower regeneration energy demand.⁷⁻¹²

An interesting class of amines for this application are derivatives of triacetoneamine. This class of amines was revealed for the first time recently in patents of Evonik.^{13,14} The amines

from that class are abbreviated by the acronym EvA. The number behind EvA designates the derivate and was introduced in a screening by Evonik. Little is known in the open literature on the thermodynamic properties of the EvAs and their aqueous solutions. In a recent work, we have studied unloaded and CO₂-loaded aqueous solutions of *n*-butyl-triacetonediamine (EvA02).¹⁵ This work is extended here to N,N-dimethyl-dipropylene-diamino-triacetonediamine (EvA34). The structural formula of EvA34 is shown in Figure 1. Experimental studies of pure EvA34 as well as of unloaded and CO₂-loaded aqueous solutions of EvA34 were carried out. The studied properties are: density ρ , liquid heat capacity c_p , vapor pressure p^s , viscosity η , CO₂ solubility p_{CO_2} , dissociation constants $\text{p}K$, pH-value pH, and loadings of CO₂-containing species $\tilde{\alpha}_i$. Table 1 gives an overview of the studied conditions. About 750 experimental data points are reported in the present work. The new data are compared to corresponding data for aqueous solutions of two amines that are widely used for CO₂ capture: monoethanolamine (MEA) and a blend of methyl-diethanolamine and piperazine (MDEA/PZ). The aim of this comparison is to evaluate the potential of the newly developed amine EvA34 as an aqueous solution for the reactive absorption of CO₂.

Experiments

Chemicals

EvA34 (Figure 1) was provided by Evonik. The amine was synthesized from the reactants N,N-dimethyl-dipropylene-triamine and 2,2,6,6-tetramethyl-4-piperidone by reductive amination using a noble metal catalyst.^{16,17} After hydrogenation at elevated temperature and pressure, EvA34 was purified by vacuum distillation and filtration. The resulting purity was controlled by GC-MS and was ≥ 0.97 g/g. Major observed impurities are 2,2,6,6-tetramethyl-4-piperidone or 2,2,6,6-tetramethyl-4-piperidinol with amounts < 0.02 g/g, and H₂O < 0.01 g/g (Karl-Fischer titration). H₂O was purified by ion-exchange and filtration with a Siemens TWF/EI-Ion UV Plus water purification system. All other chemicals were purchased and

used without further purification. Table 2 gives a survey of all chemicals that were used in the present work. The presence of impurities is not considered in the estimates of experimental uncertainties.

Sample preparation

Aqueous solutions of amines

Aqueous solutions of amines were prepared gravimetrically in this work. Dissolved gases were removed from the pure components H_2O and EvA34 by lowering the pressure with a vacuum pump. The degassed components were mixed while maintaining the low pressure. The amounts of EvA34 and H_2O in the unloaded aqueous solution were determined with an accuracy of ± 1 mg. From this, the molality of EvA34 $\tilde{m}_{\text{EvA34}}$ is known with a relative expanded uncertainty of $U_r(\tilde{m}_{\text{EvA34}}) = 0.001$ (0.99 level of confidence). In the symbols that are used to characterize compositions in the present work, the tilde refers to the pure components amine and H_2O without accounting the chemical reactions and their products.

CO_2 -loaded aqueous solutions of amines

In most experiments, the aqueous solutions of amines were loaded with CO_2 in stainless steel cylinders. The amount of aqueous solution of amine as well as the amount of CO_2 were determined by differential weighing. The accuracy of the weighing was ± 1 mg. The resulting relative expanded uncertainty in the molality of CO_2 $\tilde{m}_{\text{CO}_2}$ is $U_r(\tilde{m}_{\text{CO}_2}) = 0.01$ (0.99 level of confidence). However, for the experiments in which stainless steel cylinders with a riser pipe were used for the CO_2 -loading, incomplete mixing may have led to an underestimation of the actual molality of CO_2 . More details on this are given in the Supporting Information. The relative expanded uncertainties stated in the present work account for possible effects from incomplete mixing. They are $U_r(\tilde{m}_{\text{CO}_2}) = 0.025$ (0.99 level of confidence).

All molalities of CO_2 stated in this work were calculated from initial weighing except those for the NMR experiments. For the NMR experiments, CO_2 -loadings $\tilde{\alpha}_{\text{CO}_2}$ were directly

obtained from the NMR spectra. Relations between different properties that are used for characterizing the CO₂ content of the solution are given in Equation (1) and (2)

$$\tilde{\alpha}_{\text{CO}_2} = \frac{\tilde{m}_{\text{CO}_2}}{\tilde{m}_{\text{Amine}}} \quad (1)$$

$$\tilde{X}_{\text{CO}_2} = \tilde{\alpha}_{\text{CO}_2} \cdot \frac{M_{\text{CO}_2}}{M_{\text{Amine}}} \quad (2)$$

where $\tilde{\alpha}_{\text{CO}_2}$ is the mole-related CO₂-loading, $\tilde{m}_{\text{CO}_2}$ is the molality of CO₂, $\tilde{m}_{\text{Amine}}$ is the molality of the amine, $\tilde{X}_{\text{CO}_2}$ is the mass-related CO₂-loading, and M_{CO_2} and M_{Amine} are the molar masses of CO₂ and the amine, respectively. In these symbols, the tilde refers to the pure components CO₂, the amine, and H₂O without accounting the chemical reactions and their products.

Gas solubility

Head space gas chromatography

The partial pressure of CO₂ in the gas phase above CO₂-loaded aqueous solutions of EvA34 was measured with head space gas chromatography for pressures below 100 kPa. The equipment and the experimental procedure were the same as employed in previous works of our group^{15,18,19} and are therefore not described here in detail. The composition of the liquid phase was known from sample preparation and the partial pressure of CO₂ was determined by gas chromatography. The gas chromatograph (Agilent, type 6890) was equipped with a capillary column (J&M Scientific, type GS-Q, 30 m, 0.32 mm i.d.) and a thermal conductivity detector. For calibration, the sample cells were filled with pure CO₂ at a pressure ranging from 5 to 90 kPa. The calibration was performed before and after each change of temperature. The temperature was measured with calibrated platinum resistance thermometer in the thermostating liquid surrounding the cells. At least four sample cells were prepared and

studied in the same way. The arithmetic mean values of the measured partial pressures of CO_2 are reported here as the result.

The standard uncertainty of the measured partial pressure of CO_2 is calculated from the standard deviation of the repeated measurements and the standard uncertainty from calibration. The expanded uncertainty of the liquid composition is the same as specified in the sample preparation paragraph. The expanded uncertainty of the temperature measurement is $U(T) = 0.1 \text{ K}$ (0.99 level of confidence).

High pressure view cell

A thermostatted high pressure view cell was used to determine the bubble point pressure of CO_2 -loaded aqueous solutions of EvA34 for pressures between 0.1 and 10 MPa. The equipment and the experimental procedure were the same as in previous works of our group^{15,18,19} and are therefore not described here in detail. The bubble point pressure was measured with calibrated high precision pressure transducers from WIKA. The view cell's temperature was measured with calibrated platinum resistance thermometer in the thermostating liquid surrounding the view cell. Each experiment was repeated three times. The arithmetic mean values of the measured bubble point pressures are reported here as the result.

The standard uncertainty of the measured bubble point pressure is calculated from the standard deviation of the repeated measurements and the standard uncertainty from calibration. The expanded uncertainty of the molality of EvA34 is considered to be the same as specified in the sample preparation paragraph. CO_2 was added separately into the cell. The amount of CO_2 was known from weighing with an accuracy of $\pm 1 \text{ mg}$. The resulting relative expanded uncertainty of the molality of CO_2 is $U_r(\tilde{m}_{\text{CO}_2}) = 0.001$ (0.99 level of confidence). The expanded uncertainty of the temperature measurement is $U(T) = 0.1 \text{ K}$ (0.99 level of confidence).

Chemical equilibrium

Titration

Titration experiments were performed with a Metrohm Ti-Touch 916 Titrino, equipped with a Dosino 800. In the experiments EvA34, H₂O, and 1M HCl solution were mixed in a double jacket thermostatted and stirred vessel. After reaching the desired temperature, 1M NaOH was titrated to the mixture. The pH-value was measured with a Metrohm LL Unitrode. The pH-electrode also contained a calibrated Pt1000 that was used for the temperature measurement. The pH-electrode was calibrated with five buffer solutions at pH = 2, 6, 8, 10, and 12 before and after each temperature change. Each experiment was performed twice. The arithmetic mean values of the obtained molal activity based pK -values are reported here as the result.

The standard uncertainty of the measured pK -value is calculated from the standard deviation of the repeated measurements and the standard uncertainty from calibration. The expanded uncertainty of the temperature measurement is $U(T) = 0.1$ K (0.99 level of confidence). All titrations were performed at ambient pressure.

pH-meter

The pH-value of unloaded and CO₂-loaded aqueous solutions of EvA34 was measured with a Mettler Toledo HA405-DXK-S8 pH-electrode connected to a Mettler Toledo Five Easy FE20 pH/mV bench meter. The pH-electrode was screwed into a pressure resistant and hermetically closed stainless steel vial containing the sample. The vial was placed into an oil bath and thermostatted by the surrounding oil. The temperature of the oil bath was measured by a calibrated digital probe thermometer from TFA Dostmann (TFA 30.1021). For an experiment with unloaded aqueous solutions of EvA34, the temperature was first kept at 298.15 K for 15 minutes. Then the temperature was increased to 313.15 K for 30 minutes, followed by 353.15 K and 393.15 K for 40 minutes each. For CO₂-loaded aqueous

solutions of EvA34, the periods were: 20 minutes at 293.15 K and 120 minutes at 333.15 K and 373.15 K respectively. These timings ensured that at each temperature the thermal and chemical equilibrium was reached. The pH-electrode was calibrated with 0.01 M HCl, 0.01 M KOH, 0.1 M KOH, and $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ ²⁰ reference solutions using the same measurement procedure as described above. The molal activity based pH-value of the reference solutions was calculated using Pitzer’s extended Debye-Hückel law.²¹ Each experiment with unloaded aqueous solutions of EvA34 was performed three times. The experiments with CO_2 -loaded aqueous solutions of EvA34 were performed twice. The arithmetic mean values of the measured molal activity based pH-values are reported here as the result.

The standard uncertainty of the measured pH-value is calculated from the standard deviation of the repeated measurements and the standard uncertainty from calibration. The expanded uncertainty of the molality of EvA34 and CO_2 are considered to be the same as specified in the sample preparation paragraph. The expanded uncertainty of the temperature measurement is $U(T) = 0.1 \text{ K}$ (0.99 level of confidence). The pressure inside the vials was not measured as it has no significant influence on the measured pH-value.

NMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was used for the elucidation and quantification of the speciation in the CO_2 -loaded aqueous solutions of EvA34. The measurements were carried out with a Bruker Ascend 400 MHz spectrometer equipped with an Avance 3 HD 400 console and either CPPBBO or PABBO 5mm probe heads. All samples were analyzed in pressure resistant valved NMR tubes (S-5-400-MW-IPV-7 by Norell and 522-QPV-7 / 524-QPV-7 by Wilmad-LabGlass). The filling level inside the tubes was kept below 6 cm to ensure homogeneous thermostatisation of the liquid phase inside the NMR tube. The temperature of the samples was controlled by a thermostatted nitrogen gas flow in the NMR spectrometer. The temperature was calibrated by using the temperature dependent ^1H shift of methanol (288.15 K to 333.15 K) and ethylene glycol (353.15 K to 393.15 K).²² To reach

chemical equilibrium, the samples were thermostatted for 4 hours in an oven before they were analyzed in the NMR.

For the elucidation ^1H , $^{13}\text{C}\{^1\text{H}\}$ inverse gated, and two-dimensional ^1H - ^{13}C heteronuclear single quantum coherence (HSQC), ^1H - ^{13}C heteronuclear multiple bond correlation (HMBC), and 135° distortionless enhanced polarization transfer ^{13}C (DEPT135) measurements were used.

For the quantification of the CO_2 -containing species, $^{13}\text{C}\{^1\text{H}\}$ inverse gated NMR spectra (decoupling sequence: waltz16, flip angle: 30° or 60° , relaxation delay: 60 s, acquired size of FID: 128k, sweep width: 220 ppm, excitation frequency offset: 100 ppm, acquisition time: 2.97 s, 128 to 1024 scans per spectra) were applied. A preliminary variation of acquisition parameters and T_1 measurements ($T_1 \leq 7$ sec) proved the applicability of the listed parameters for this system. The recorded spectra were post-processed manually (zero filling, line broadening, phase correction, Whittaker-Smoother baseline correction). The peak areas were determined by direct integration. The results were taken from comparing the peak integrals of the different CO_2 -containing species and expressed as loadings of CO_2 -containing species $\tilde{\alpha}_i$ of the species i related to the total amount of EvA34. The overall CO_2 -loading was calculated from the loadings of CO_2 -containing species as shown in Equation (3). In the symbols that are used to characterize the loadings of CO_2 -containing species in the present work, the tilde refers to the measured amounts of the species and include all protonated forms of the species. Each sample was measured once at each temperature.

$$\tilde{\alpha}_{\text{CO}_2} = \sum_i \tilde{\alpha}_i \quad (3)$$

The values listed in Table 3 are taken to describe the standard uncertainty of the measured loadings of CO_2 -containing species. They result mainly from uncertainties in the post-processing and peak integration. The expanded uncertainty of the molality of EvA34 is considered to be the same as specified in the sample preparation paragraph. The expanded uncertainty of the temperature measurement is $U(T) = 0.1$ K (0.99 level of confidence). The

pressure inside the NMR tubes was not measured as it has no significant influence on the measured loading of CO₂-containing species.

Liquid heat capacity

The liquid heat capacity c_p of pure EvA34 and its mixtures with H₂O was measured in a differential scanning calorimeter (DSC) Q2000 from TA Instruments. The temperature measurement of the DSC was calibrated using melting point determination. The cell's heat flux was calibrated by melting enthalpy calibration. The heat capacity measurement was calibrated with a sapphire standard (No. 915079.902) provided by TA Instruments. For weighing the samples, a Mettler Toledo MX5 was used. For all experiments, hermetically closed Tzero Alodined pans and lids from TA Instruments were used. The pans and lids were passivated to avoid the base catalyzed formation of aluminum-hydroxide and hydrogen.

For the measurement an upward temperature ramp of 5 K/min between 293.15 K and 353.15 K was applied. Each sample was measured three times in a row. Before and between each run a resting time of 5 minutes at 293.15 K was given. The result of the first run was discarded. The average of the second and third run is reported here as the measured liquid heat capacity.

The standard uncertainty of the measured liquid heat capacity is calculated from the standard deviation of the repeated measurements and the standard uncertainty from calibration. The expanded uncertainty of the molality of EvA34 is considered to be the same as specified in the sample preparation paragraph. The expanded uncertainty of the temperature measurement is $U(T) = 0.1$ K (0.99 level of confidence). The pressure inside the pans was not measured as it has no significant influence on the measured liquid heat capacity.

Density and dynamic viscosity

The density and dynamic viscosity of unloaded and CO₂-loaded aqueous solutions of EvA34 were measured with an Anton Paar SVM 3000 instrument which is a combination of an

oscillating U-tube densimeter and Stabinger viscosimeter. Each experiment was repeated up to five times. The arithmetic mean values of the measured densities and dynamic viscosities are reported here as the result.

The standard uncertainty of the measured density and dynamic viscosity is calculated from the standard deviation of the repeated measurements and the standard uncertainty from calibration. The expanded uncertainty of the molality of EvA34 and CO₂ are considered to be the same as specified in the sample preparation paragraph. The expanded uncertainty of the temperature measurement is $U(T) = 0.1$ K (0.99 level of confidence). The measurements were performed at ambient pressure.

Vapor pressure

The vapor pressure of pure EvA34 was measured in a circulation still.^{23,24} In the apparatus, the pressure was set and the temperature was measured. The pressure was measured with a P-30 0.1 MPa full scale high precision capacitive pressure sensor from WIKA. The temperature was measured with a calibrated Pt100 thermometer. Due to the onset of carbonization at temperatures above 488.15 K, only low pressures could be studied. The pressure and temperature were recorded every 5 seconds for 30 minutes. The arithmetic mean values of the pressure and temperature are reported here as the result.

The standard uncertainty of the measured pressure and temperature is calculated from the standard deviation of the recorded pressure and temperature and the standard uncertainty from pressure and temperature calibration.

Experimental results

Gas solubility

The CO₂ solubility at 313.15 K, 353.15 K, and 393.15 K from head space gas chromatography and from high pressure view cell experiments are presented in Figure 2. In the diagrams the

partial pressure of CO₂ p_{CO_2} is shown as a function of the CO₂-loading $\tilde{\alpha}_{\text{CO}_2}$ for aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g and $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g, respectively. The partial pressures of CO₂ from head space gas chromatography experiments are directly used in the diagrams. The partial pressures of CO₂ from high pressure view cell experiments are calculated from the measured bubble point pressure in the same way as described in a previous work of our group.¹⁸

The displayed isotherms show a parallel shape in most regions of both diagrams. The isotherms for $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g below a partial pressure of CO₂ of 0.5 MPa however differ clearly in their shape. The isotherm at 313.15 K shows a convex profile, the isotherm at 393.15 K a concave. The resulting large difference between the two isotherms is beneficial for absorption/desorption processes. The corresponding numerical data are presented in the Supporting Information.

Chemical equilibrium

p*K*-values

Figure 3 shows an exemplary result from a titration experiment of highly diluted EvA34 at 313.15 K. The measured pH of the titration curve and its first derivative are shown as a function of the added volume of 1M NaOH titrant $V_{\text{1M NaOH}}$. The equivalent points EP1, EP2, EP3, and EP5 are taken at the turning points of the first derivative. EP4 can not be determined directly from the first derivative. It is calculated by assuming equivalent volumes of titrant between every equivalent point. The p*K*-values are determined at the mean added volumes of titrant between two adjacent equivalent points.²⁵

Figure 4 shows the p*K*-values, determined by titration experiments at 293.15 K, 313.15 K, 333.15 K, and 353.15 K. The p*K*-values are designated using the nitrogen atom (N-atom) labeling from Figure 1. The highest p*K*-value is assigned to the α -N-atom of EvA34 according to the literature.^{15,26,27} The second highest p*K*-value is assigned to the δ -N-atom. Literature data for dimethyl-propylamines^{28,29} and the far distance to the firstly protonated

α -N-atom support this assignment. The third highest pK -value is assigned to the β -N-atom, and the lowest pK -value to the γ -N-atom. Arguments for these assignments are the larger inductive effect of the piperidine ring at the β -N-atom compared to the γ -N-atom, literature data¹⁵ for a similar β -N-group arrangement, and negligible influence of the steric hindrance.^{26,29,30} The numerical data are presented in the Supporting Information.

pH-values of unloaded aqueous solutions of EvA34

Figure 5 shows the pH-values as a function of the mass fraction of EvA34 in the unloaded aqueous solutions $\tilde{w}_{\text{EvA34}}^0$ at 298.15 K, 313.15 K, 353.15 K, and 393.15 K from pH-value measurements. Compared to other solvents that are often used for CO₂ absorption,^{4,18,31} the obtained pH-values of aqueous solutions of EvA34 are remarkably high. The corresponding data are presented in the Supporting Information.

Elucidation of CO₂-containing species

Figure 6 shows the CO₂-containing species in the system EvA34, CO₂ and H₂O that were observed by NMR spectroscopy in the present work. The elucidation is described in the Supporting Information. CO₂ reacts with both, the β - and γ -N-atom of EvA34 to form carbamates (cf. Figure 1). Also (bi-)carbonate is found.

Protonated and unprotonated species cannot be distinguished in NMR spectra. Depending on the pH-value, differently protonated species of the carbamates/carbonates arise. The carbamates are designated β -COO⁻, γ -COO⁻ and β - γ -(COO⁻)₂ in this work, with the greek letter giving information about the carbamate position. These designations include all protonation-states of the corresponding species here. Carbonate and bicarbonate is lumped together and labeled H_xCO₃.

Loadings of CO₂-containing species

Figure 7 shows the loadings of CO₂-containing species for aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g and $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g at 293.15 K from NMR experiments. In the figure the loadings of CO₂-containing species $\tilde{\alpha}_i$ (with $i = \beta\text{-COO}^-$, $\gamma\text{-COO}^-$, $\beta\text{-}\gamma\text{-(COO}^-)_2$, H_xCO_3) are shown as a function of the CO₂-loading $\tilde{\alpha}_{\text{CO}_2}$.

The major carbamate species is $\gamma\text{-COO}^-$. The loadings of $\beta\text{-COO}^-$ and $\beta\text{-}\gamma\text{-(COO}^-)_2$ are small. The loadings of $\beta\text{-COO}^-$ and $\gamma\text{-COO}^-$ increase with increasing CO₂-loading until they reach a maximum value which does not change significantly upon a further increase of the CO₂-loading. Aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g reach this maximum at a lower CO₂-loading than solutions with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g. For aqueous solutions with $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g, $\beta\text{-}\gamma\text{-(COO}^-)_2$ is only observed at high CO₂-loadings. The loading of $\beta\text{-}\gamma\text{-(COO}^-)_2$ as a function of the CO₂-loading shows a maximum. No $\beta\text{-}\gamma\text{-(COO}^-)_2$ is found in aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g.

With increasing temperature, the loadings of carbamates decrease. This decrease is demonstrated in Figure 8 where the loadings of $\gamma\text{-COO}^-$ $\tilde{\alpha}_{\gamma\text{-COO}^-}$ are shown as a function of the CO₂-loading $\tilde{\alpha}_{\text{CO}_2}$ for aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g and $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g at different temperatures. The decrease of the loadings of $\gamma\text{-COO}^-$ with increasing temperature is stronger for $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g than for $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. For $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g, a significant decrease is only observable at 373.15 K and 393.15 K. The same observations are made for the loadings of $\beta\text{-COO}^-$ and $\beta\text{-}\gamma\text{-(COO}^-)_2$. The numerical data are presented in the Supporting Information.

pH-values of CO₂-loaded aqueous solutions of EvA34

Figure 9 shows the pH-value of CO₂-loaded aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g and $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g at 293.15 K, 333.15 K, and 373.15 K as a function of the CO₂-loading $\tilde{\alpha}_{\text{CO}_2}$ from pH-value measurements. The pH-value decreases almost linearly with

increasing CO₂-loading except for very small loadings. The numerical data are presented in the Supporting Information.

Liquid heat capacity

In Figure 10 the liquid heat capacity c_p of unloaded aqueous solutions of EvA34 from DSC experiments is presented as a function of the EvA34 mass fraction in the unloaded aqueous solution $\tilde{w}_{\text{EvA34}}^0$ for temperatures between 298.15 K and 348.15 K. A maximum of the liquid heat capacity is observable at about $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g. However, the increase of the heat capacity in that maximum compared to that of water is small and does not exceed the experimental standard uncertainty. The liquid heat capacity of pure EvA34 is between 2.05 kJ/(kg·K) at 298.15 K and 2.25 kJ/(kg·K) at 348.15 K. The corresponding numerical data are given in the Supporting Information.

Density

Figure 11 shows the density ρ of aqueous solutions of EvA34 as a function of the EvA34 mass fraction in the unloaded aqueous solution $\tilde{w}_{\text{EvA34}}^0$ from density measurements for temperatures between 293.15 K and 353.15 K. For the lowest studied temperatures, a maximum in the density at about $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g is observable. The maximum relative increase of the density is 0.7 % compared to pure H₂O and is found for 293.15 K.

Figure 12 shows the density ρ of CO₂-loaded aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g and $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g as a function of the CO₂-loading $\tilde{\alpha}_{\text{CO}_2}$ for temperatures between 293.15 K and 353.15 K. The density increases almost linearly with increasing CO₂-loading. The corresponding numerical data are presented in the Supporting Information.

Dynamic viscosity

Figure 13 shows the dynamic viscosity η of unloaded aqueous solutions of EvA34 as a function of the EvA34 mass fraction in the unloaded aqueous solution $\tilde{w}_{\text{EvA34}}^0$ at temperatures between 293.15 K and 353.15 K. The dynamic viscosity of pure EvA34 is between 63 mPa·s at 293.15 K and 5 mPa·s at 353.15 K. There is a maximum of the dynamic viscosity at about $\tilde{w}_{\text{EvA34}}^0 = 0.8$ g/g. This value equals a ratio between H₂O-molecules and N-atoms of 1/1. The maximum values are 1829 mPa·s at 293.15 K and 13.7 mPa·s at 353.15 K. It can be assumed that H-bond-stabilized clusters are formed between EvA34 and H₂O that cause this strong increase in the dynamic viscosity.

The dynamic viscosity is very sensitive to the mass fraction of H₂O. One of the impurities of EvA34 is H₂O (see section Chemicals). Even though the amount of H₂O as an impurity in pure EvA34 is low (less than 0.01 g/g), it might have an influence on the measured dynamic viscosity. This should be kept in mind when the absolute values of the dynamic viscosity are regarded. The general interpretation and conclusions, made from the results, however retain their validity.

Figure 14 shows the dynamic viscosity η of CO₂-loaded aqueous solutions of EvA34 as a function of the CO₂-loading $\tilde{\alpha}_{\text{CO}_2}$ for aqueous solutions of EvA34 with $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g and $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g and temperatures between 293.15 K and 353.15 K. The influence of the CO₂-loading on the dynamic viscosity is small for $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g. However, for $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g an increase of the dynamic viscosity is observable with increasing CO₂-loading. The slope of the increase changes at a CO₂-loading of about $\tilde{\alpha}_{\text{CO}_2} = 1.5$ mol/mol. A comparison of the results that are shown in Figure 7 and Figure 14 indicates that this change of the slope could be related to the influence of the carbamates. The corresponding numerical data are presented in the Supporting Information

Vapor pressure

Figure 15 shows the vapor pressure of pure EvA34 p_{EvA34}^s as a function of the temperature T . Compared to other amines that are used for CO_2 absorption,⁴ EvA34 has a very low vapor pressure. The numerical data are presented in the Supporting Information.

Comparison of EvA34 with MEA and MDEA/PZ

A comparison of the experimental results for EvA34 with literature data for monoethanolamine (MEA) and a mixture of methyl-diethanolamine (MDEA) and piperazine (PZ with a mass ratio of 7/1 (MDEA/PZ) is presented in this chapter. MEA is a common primary amine and often used as a reference in studies of solvents for CO_2 absorption. Mixtures of MDEA and PZ are commonly used for the CO_2 absorption from synthesis gas and can be seen as a benchmark in that field.^{4,32} In the following comparison, pure component data and data for aqueous amine solutions with $\tilde{w}_{\text{Amine}}^0 = 0.4$ g/g are discussed. Two temperatures are considered: 313.15 K and 393.15 K. These conditions are chosen because of their relevance for the industrial application.

A comparison of the pure component vapor pressure p^s , as well as of the liquid heat capacity c_p and dynamic viscosity η of EvA34, MEA, MDEA/PZ, and its aqueous solutions is shown in Table 4. The vapor pressure of EvA34 is extrapolated from the measured data.

The low vapor pressure of EvA34 compared to MEA and MDEA/PZ minimizes solvent losses in absorption/desorption processes. The viscosity of aqueous solutions of EvA34 is significantly higher than those of MEA and MDEA/PZ. The addition of CO_2 further increases the viscosity (see Figure 14).^{33,34} Higher viscosities typically have negative influence on the mass transfer and reduce the rate of absorption.³⁵ The slightly higher liquid heat capacity of aqueous solutions of EvA34 is not relevant for the energy demand of absorption/desorption processes.

Figure 16 shows a comparison of the CO_2 solubility and the chemical equilibrium of the three considered solvents. The data for MEA and MDEA/PZ is generated from the model of Wagner et al.¹⁸ and Ermatchkov et al.,³¹ respectively. The upper row of diagrams shows the partial pressure of CO_2 p_{CO_2} . The lower row shows the amount of CO_2 chemically bound as carbamates in relation to the amount of CO_2 that is chemically bound as carbamates and carbonates: the carbamate ratio ξ_{CARB} . Both values are depicted as a function of the mass-related CO_2 -loading $\tilde{X}_{\text{CO}_2}$.

The CO_2 solubility in aqueous solutions of EvA34 and MEA at 313.15 K is significantly higher than in aqueous solutions of MDEA/PZ. This is beneficial since the absorption rate increases and the amount of solvent needed for a given purification task decreases. At low CO_2 partial pressures, the high CO_2 solubility is favorable to achieve low residual amounts of CO_2 in the gas streams. This is important e.g. in synthesis gas purification, where CO_2 partial pressures down to a few ppm are targeted. In this region, EvA34 fails MEA but exceeds MDEA/PZ.

The CO_2 solubility in aqueous solutions of EvA34 and MDEA/PZ at 393.15 K is much lower than in aqueous solutions of MEA. EvA34 and MDEA/PZ differ slightly in the higher CO_2 partial pressure region, where the CO_2 solubility of MDEA/PZ is even lower than that of EvA34. A low CO_2 solubility reduces the amount of stripping steam required for the regeneration as more CO_2 flashes from the solvent just because of the pressure drop and temperature increase between absorber and desorber. The reduction of stripping steam lowers the energy demand for the solvent regeneration.

The ratio of CO_2 that is chemically bound as carbamates at 313.15 K and 393.15 K is much higher for aqueous solutions of MEA than for aqueous solutions of EvA34 and MDEA/PZ. At 313.15 K EvA34 forms more carbamates than MDEA/PZ. At 393.15 K the ratios of EvA34 and MDEA/PZ are similar. The formation of carbamates is faster than the formation of carbonates. Fast reactions are favorable for the absorption. However, the regeneration of carbamates demands more energy than the regeneration of carbonates.^{2,9,36-38}

For an absorption/desorption process, EvA34 combines the favorable properties of MEA and MDEA/PZ in one molecule. EvA34 shows both, high CO₂ solubility at absorption conditions and low CO₂ solubility at desorption conditions. The large difference between the CO₂ solubilities of EvA34 at 313.15 K and 393.15 K compared to MEA and MDEA/PZ allows to reduce the amount of solvent needed for a given purification task. Furthermore it gives the opportunity to operate EvA34 at higher equilibrium loadings in both, absorber and desorber to reduce the amount of stripping steam needed for the regeneration. Finally, the wide operation window gives flexibility for adjusting process conditions. E.g. the temperature could be increased, which would lead to a lower viscosity and improved mass transfer kinetics.

Conclusion

Results from a comprehensive study of physico-chemical properties for the triacetoneamine-derivative EvA34 are presented in this work. CO₂ solubility, chemical equilibrium, density, viscosity, vapor pressure, and liquid heat capacity for the pure amine, aqueous solutions, and CO₂-loaded aqueous solutions were measured. A comparison to literature data for MEA and MDEA/PZ shows that aqueous solutions of EvA34 are interesting solvents for reactive CO₂ absorption/desorption processes. For the evaluation of this potential, pilot plant experiments and a reliable thermodynamic equilibrium model is required. The experimental data presented in this work provide the information to build such a model.

Acknowledgment

We gratefully acknowledge the financial support of this work by the Federal Ministry of Economic Affairs and Energy of the Federal Republic of Germany (grant no. 03ET1098) and by Evonik and thyssenkrupp.

Supporting Information Available

- Uncertainty of the gravimetric determination of the CO₂-loading.
- Species elucidation of unloaded and CO₂-loaded aqueous solutions of EvA34.
- Numerical experimental data.

Tables

Table 1: Overview of experiments of the present work. $\tilde{w}_{\text{EvA34}}^0$: mass fraction of EvA34 in the unloaded aqueous solution, $\tilde{\alpha}_{\text{CO}_2}$: CO₂-loading, p : pressure, T : temperature, p_{CO_2} : partial pressure of CO₂, $\text{p}K$: dissociation constants, pH : molal activity of H⁺, $\tilde{\alpha}_i$: CO₂ species distribution, c_p : liquid heat capacity, ρ : density, η : dynamic viscosity, p^s : vapor pressure, amb: ambient pressure.

property	$\tilde{w}_{\text{EvA34}}^0$ g/g	$\tilde{\alpha}_{\text{CO}_2}$ mol/mol	p MPa	T K	data points
p_{CO_2}	0.1	0.3 - 2.8	0.002 - 0.074	313.15 - 393.15	20
	0.4	0.1 - 2.7	0.002 - 0.081	313.15 - 393.15	31
	0.1	2.1 - 6.2	0.51 - 7.32	313.15 - 393.15	22
	0.4	1.2 - 3.7	0.15 - 8.83	313.15 - 393.15	29
$\text{p}K$	0.01	-	amb	293.15 - 353.15	36
pH	0.001 - 0.4	-		298.15 - 393.15	36
	0.1	0.3 - 2.6		293.15 - 373.15	24
	0.4	0.3 - 2.6		293.15 - 373.15	25
$\tilde{\alpha}_i$	0.1	0.2 - 3.1		293.15 - 353.15	31
	0.4	0.1 - 3.3		293.15 - 393.15	56
c_p	0.1 - 1.0	-		298.15 - 348.15	48
ρ	0.1 - 1.0	-	amb	293.15 - 353.15	105
	0.1	0.9 - 2.8	amb	293.15 - 353.15	25
	0.4	0.1 - 2.0	amb	293.15 - 353.15	59
η	0.1 - 1.0	-	amb	293.15 - 353.15	105
	0.1	0.9 - 2.8	amb	293.15 - 353.15	25
	0.4	0.1 - 2.0	amb	293.15 - 353.15	59
p^s	1.0	-	0.002 - 0.005	473.15 - 486.15	4

Table 2: Chemicals that were used in the present work.

name (CAS)	source	initial	purification	final	analysis
		purity	method	purity	method
EvA34 (-)	Evonik	0.97 ^b		0.97 ^b	^g
H ₂ O (7732-18-5)	SWK ^d		^c	0.99999 ^b	^f
CO ₂ (124-38-9)	Air Liquide	0.99995 ^a		0.99995 ^a	^e
MEA (141-43-5)	Sigma-Aldrich	0.99 ^b		0.99 ^b	^e
MDEA (105-59-9)	Sigma-Aldrich	0.99 ^b		0.99 ^b	^e
PZ (110-85-0)	Sigma-Aldrich	0.99 ^b		0.99 ^b	^e
1 M HCl (7647-01-0)	Carl Roth	0.998 ^a		0.998 ^a	^e
1 M NaOH (1310-73-2)	Carl Roth	0.998 ^a		0.998 ^a	^e
KOH (1310-58-3)	Fluka	0.99 ^b		0.99 ^b	^e
KH ₂ PO ₄ (7778-77-0)	Bernd Kraft	0.99 ^b		0.99 ^b	^e
Na ₂ HPO ₄ (7558-79-4)	Bernd Kraft	0.99 ^b		0.99 ^b	^e
Titrisol pH-buffer (-)	Merck				

^a mole fraction

^b mass fraction

^c ion-exchange and filtration

^d Stadtwerke Kaiserslautern

^e stated by supplier

^f conductometry

^g GC-MS and Karl-Fischer titration

Table 3: Standard uncertainty of the quantitative NMR investigation. $\tilde{w}_{\text{EvA34}}^0$: mass fraction of EvA34 in the unloaded aqueous solution, $\tilde{\alpha}_i$: loading of CO₂-containing species, T : temperature, u : standard uncertainty, u_r : relative standard uncertainty.

$\tilde{w}_{\text{EvA34}}^0$	T	$u_r(\tilde{\alpha}_i) ; u(\tilde{\alpha}_i)$
g/g	K	- ; mol/mol
0.1	273.15 - 333.15	$\max\{ 0.05 ; 0.03 \}$
0.4	273.15 - 333.15	$\max\{ 0.03 ; 0.02 \}$
0.1 & 0.4	353.15 - 393.15	$\max\{ 0.08 ; 0.05 \}$

Table 4: Properties of EvA34, MEA, MDEA/PZ and their aqueous solutions. T : temperature, $\tilde{w}_{\text{Amine}}^0$: mass fraction of the amine in the unloaded aqueous solution, c_p : liquid heat capacity, η : dynamic viscosity, p^s : vapor pressure.

	T	$\tilde{w}_{\text{Amine}}^0$	EvA34	MEA	MDEA/PZ
	K	g/g			
$c_p / \text{kJ}/(\text{kg}\cdot\text{K})$	313.15	0.4	3.86 ^a	3.63 ³⁹	3.55 ⁴⁰
		1.0	2.11 ^a	2.78 ⁴¹	2.35 ⁴⁰
$\eta / \text{mPa}\cdot\text{s}$	313.15	0.4	10.7 ^a	2.3 ⁴²	3.5 ^a
		1.0	18.9 ^a	9.6 ⁴²	45.1 ^a
p^s / kPa	393.15	1.0	$\leq 0.002^b$	16.33 ⁴³	0.98 ⁴³ /16.28 ⁴⁴
^a this work					
^b extrapolated from data of this work					

Figures

Figure 1: Structural formula of EvA34. Greek letters are used for designating the four nitrogen atoms.

Figure 2: CO_2 solubility in aqueous solutions of EvA34. Experimental results from the present work. Left: $\tilde{w}_{\text{EvA34}}^0 = 0.1 \text{ g/g}$, right: $\tilde{w}_{\text{EvA34}}^0 = 0.4 \text{ g/g}$. O: from head space gas chromatography, $\diamond$: from high pressure view cell. Blue: 313.15 K, gray: 353.15 K, red: 393.15 K.

Figure 3: Exemplary result of a titration experiment with highly diluted EvA34 at 313.15 K. —: pH-value, —: first derivative of the pH-value, — EP: equivalent point, +: pK -value.

Figure 4: pK -values of the four amino-groups of EvA34 (cf. Figure 1). Experimental results from the present work. Δ : α -N-atom, ∇ : δ -N-atom, $\triangleright$: β -N-atom, $\triangleleft$: γ -N-atom.

Figure 5: pH-value of unloaded aqueous solutions of EvA34. Experimental results from the present work. $\diamond$: 298.15 K, $\triangle$: 313.15 K, $\circ$: 353.15 K, $\square$: 393.15 K.

Figure 6: CO_2 -containing species in CO_2 -loaded aqueous solutions of EvA34. Experimental results from the present work. Greek letters indicate the position of the carbamate group corresponding to the designation in Figure 1.

Figure 7: Loadings of CO_2 -containing species in CO_2 -loaded aqueous solutions of EvA34 at 293.15 K. Experimental results from the present work. Left: $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g, right: $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. $\diamond$: $\gamma\text{-COO}^-$, $\triangle$: $\beta\text{-COO}^-$, $\circ$: $\beta\text{-}\gamma\text{-(COO}^-)_2$, ∇ : H_xCO_3 .

Figure 8: Temperature dependence of the loadings of $\gamma\text{-COO}^-$. Experimental results from the present work. Left: $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g, right: $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. $\diamond$: 293.15 K, $\triangle$: 313.15 K, ∇ : 333.15 K, $\circ$: 353.15 K, $\triangleleft$: 373.15 K, $\square$: 393.15 K.

Figure 9: pH-value of CO₂-loaded aqueous solutions of EvA34. Experimental results from the present work. Left: $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g, right: $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. $\diamond$: 293.15 K, ∇ : 333.15 K, $\triangleleft$: 373.15 K.

Figure 10: Liquid heat capacity of unloaded aqueous solutions of EvA34. Experimental results from the present work. $\diamond$: 298.15 K, $\triangle$: 308.15 K, $\triangleleft$: 318.15 K, $\triangleright$: 328.15 K, $\circ$: 338.15 K, $\square$: 348.15 K.

Figure 11: Density of unloaded aqueous solutions of EvA34. Experimental results from the present work. $\blacklozenge$: 293.15 K, $\blacktriangle$: 303.15 K, $\blacktriangledown$: 313.15 K, $\bullet$: 333.15 K, $\blacksquare$: 353.15 K.

Figure 12: Density of CO_2 -loaded aqueous solutions of EvA34. Experimental results from the present work. Left: $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g, right: $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. $\blacklozenge$: 293.15 K, $\blacktriangle$: 303.15 K, $\blacktriangledown$: 313.15 K, $\bullet$: 333.15 K, $\blacksquare$: 353.15 K

Figure 13: Dynamic viscosity of unloaded aqueous solutions of EvA34. Experimental results from the present work. $\diamond$: 293.15 K, $\triangle$: 303.15 K, ∇ : 313.15 K, $\circ$: 333.15 K, $\square$: 353.15 K

Figure 14: Dynamic viscosity of CO_2 -loaded aqueous solutions of EvA34. Experimental results from the present work. Left: $\tilde{w}_{\text{EvA34}}^0 = 0.1$ g/g, right: $\tilde{w}_{\text{EvA34}}^0 = 0.4$ g/g. $\diamond$: 293.15 K, $\triangle$: 303.15 K, ∇ : 313.15 K, $\circ$: 333.15 K, $\square$: 353.15 K

Figure 15: Vapor pressure of pure EvA34. Experimental results from the present work.

Figure 16: Comparison of the CO_2 solubility (top row) and carbamate ratio in the liquid phase (bottom row) of aqueous solutions of amines with $\tilde{w}_{\text{Amine}}^0 = 0.4 \text{ g/g}$. Blue: 313.15 K, red: 393.15 K. $\diamond$: Experimental results from the present work, —: results generated from a model for MEA¹⁸ and MDEA/PZ.³¹

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