Solvation and Dynamics of CO2 in Aqueous Alkanolamine Solutions

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Abstract

Carbon dioxide sequestration from flue gases by chemical absorption is the most versatile process. The molecular engineering of novel high-performant biogas upgrading alkanolamine compounds requires detailed information about their properties in mixed solution. The liquid structure properties of four representative alkanolamine molecules (monoethanolamine (MEA) as a reference and standard, 3-aminopropanol (MPA), 2-methylaminoethanol (MMEA) and 4-diethylamino-2-butanol (DEAB)) in the presence of CO₂ were investigated over a wide range of solvent alkanolamine/water mixture compositions and temperature. In aqueous solution, hydrogen bonding with solvent water molecules are dominating over CO₂ interactions for MEA, MPA and MMEA. Analysis of the liquid structure reveals that carbon dioxide shows no preference of approaching the alkanolamine but is rather displaced by water molecules. CO₂ dissolved in aqueous DEAB, however, accumulates within clusters of DEAB molecules devoid of water. The carbon dioxide diffusion coefficients for all four molecules agree well with experiment for where available and are obtained for all mixture compositions and as a function of temperature. The solute diffusion correlates with the mobility of the alkanolamines in water at various ternary mixture compositions. Kinetic aspects of the CO₂-alkanolamine interactions are described by characteristic residence times of CO₂. The hydrophic interaction of carbon
dioxide with the alkanolamine has a lifetime of the order of tens of picoseconds whereas polar interactions are about one order of magnitude shorter. The tertiary amine DEAB displays many favorable features for an efficient CO$_2$ chemisorption process. Molecular engineering of novel compounds for absorbive sequestration have to take into account not only the thermodynamics and chemical reactivity but also liquid structure properties and the dynamics and kinetics of interactions in complex ternary solutions.
Introduction

Global energy consumption and demand are continuously increasing but the majority of the resources exploited like petroleum, natural gas, and coal are from fossil sources and not sustainable. Carbon dioxide emission is the major source for global warming from using fossil fuels [1] but also released as a byproduct from microbial fermentation processes, for example from biogas in a sustainable waste management. Biogas is a combination of methane (50-75%), CO$_2$ (25-50%), nitrogen (0-10%), H$_2$S (0-3%) depending on the fermentation (organic waste) and the microbial anaerobic digestion process. [2] For some applications, such as vehicle fuel or grid injection it is necessary to fulfill strictly defined specifications and therefore the natural gas needs to be upgraded.

In the final step, the separation of the mixture of CO$_2$ and CH$_4$ must be accomplished. Since CO$_2$ is the major contaminant of biogas, its removal is the most critical step in terms of economics, e.g. for transport applications or satisfying pipeline specifications. Biogas can be upgraded for removing CO$_2$ by using different technologies such as cryogenic separation, membrane separation, organic physical scrubbing, chemical scrubbing, pressure swing adsorption, and high pressure water scrubbing. [3] Reversible chemical absorption in amine-based solutions can be considered as the most advanced and promising technique for CO$_2$ capture from flue gas nowadays. [4],[5],[6] Since it accounts for 3–6% of the biomethane production cost, the absorbent material for CO$_2$/CH$_4$ gas mixture separation requires a high chemical and energy efficiency for the absorption and solvent recovery processes. The development of new CO$_2$ absorbing processes, requires the design of novel, robust and efficient physical organic absorbers.

Modern computational methods and simulations greatly contribute to solutions of such problems but have mostly focused on quantum chemical methods, for reviews see [7] and [8]. The first principles simulations of CO$_2$ binding are able to give reaction energy profiles, elucidate alternative reaction pathways and investigate the influence of chemical functional groups on solvent absorption but cannot address liquid state properties, such as viscosity, solubility and phase separations.

From a computer-based screening of compounds, a set of new and promising CO$_2$ absorptive solvents were chosen out of hundreds known and new compounds and recommended as potential based on their thermodynamic, reactive and sustainable
properties.[9] From a large set of molecular compounds, a subset was evaluated as to their thermodynamic, kinetic, and sustainability behaviour using the group-contribution statistical associating fluid theory for square well potentials (SAFT-γ SW). We here use a representative subset of four alkanolamine compounds; the well-characterized monoethanolamine (MEA) as a standard and benchmark, and three representatives for each class: a primary amine 3-aminopropanol (MPA), a secondary amine 2-methylaminoethanol (MMEA) and a tertiary amine 4-diethylamino-2-butanol (DEAB).

Figure 1. Four high-performance and sustainable alkanolamine compounds for CO₂ qeestration from biogas in their low energy conformation in aqueous solution. MEA (monoethanolamine) was used as a standard and reference compound and compared with another primary amine 3-aminopropanol (MPA), a secondary amine 2-methylaminoethanol (MMEA) and a tertiary amine 4-diethylamino-2-butanol (DEAB) as to their properties in ternary mixtures with CO₂ and water. The marked spot is used to analyze the liquid structure of complex mixtures by means of the radial density functions (RDFs).

Molecular simulations are able to generate detailed insight and data, such as thermodynamic and transport properties, for novel CO₂ absorbing compounds [8] which are not available in the literature and not accessible experimentally. For example, the diffusion coefficients of CO₂ in these absorptive alkanolamine solvents are not possible to measure experimentally because of the high reactivity in solution. Very often, one then resorts to the diffusion coefficients of N₂O in solution, for a review see [10] There is, however, recent
evidence for the validity of this CO$_2$/N$_2$O diffusion data extraction for dilute solutions only and an apparent lack of VLE data for CO$_2$ and N$_2$O. Continuous fractional component Monte Carlo (CFCMC) simulations showed that the CO$_2$/N$_2$O analogy was valid for a 30% aqueous MEA solution at 303 K. [11]

In the current paper, we are investigating the structural and dynamic features of CO$_2$ molecules in aqueous alkanolamine solutions over a wide range in temperature range and solvent compositions. Those compounds were identified previously as high-performant, non-toxic and sustainable promising novel CO$_2$ absorbing compounds.[9] The analysis gives insight into the molecular solute-solvent interactions for CO$_2$ with water and alkanolamines, the location enrichment of carbon dioxide in the vicinity of the alkanolamine molecules[12], and mobile properties of CO$_2$ in mixed solvents. [11][13] The aqueous alkanolamine system is a complex solution with competing hydophilic and hydrophobic interactions of the alkanolamine moiety and the polar water molecules.[14] The liquid structure and solvation dynamics of CO$_2$ in the simplest alkanolamine MEA and water [15] and in pure MEA [16] were investigated previously but limited to a single CO$_2$ scrubbing compound, at a single temperature and solvent composition.

We here present a systematic investigation of the structural solution and dynamic properties of CO$_2$ in aqueous solution of novel alkanolamine compounds and compare with the current standard absorber MEA. The effects of solvent composition (from pure alkanolamines towards water-rich aqueous solutions) and temperature in a temperature range of 298-323 K relevant for practical application are investigated.

Primary and secondary amines display preferential interactions with solvent water molecules and less so with carbon dioxide. In aqueous solution, CO$_2$ diffusion is fast and residence times are short. DEAB as a novel alkanolamine carbon dioxide-absorbing compound, however, displays favorable structural and kinetic features for CO$_2$ sequestration from biogas.

**Computational Methods and Details**

Alkanolamines, water and carbon dioxide were modelled using the all-atom optimized potentials for liquid simulations (OPLS-AA) forcefield[17] the charge/extended (SPC/E) model for water [18] and the transferable potentials for phase equilibria (TraPPE) force field for CO$_2$. [19] This choice of forcefields was shown to give accurate results for
alkanolamines and water solutions over a wide range of temperature and concentration. [14]. The application of the TraPPE forcefield for modelling of CO$_2$ solubility and diffusivity in water, ethanol and aqueous MEA was validate before[11]. Long-range electrostatic interactions were treated with the particle-mesh Ewald algorithm. Non-bonded interactions were modelled with a 12−6 Lennard-Jones potential. A cutoff radius of 1.4 nm was used for all interactions. Lennard-Jones parameters for unlike interactions were calculated using the geometric average rule.

MD simulations were carried out with Gromacs 5.1.2[20] in a temperature range from 298 to 323 K. The following sequence of simulation steps was performed for each alkanolamine type and aqueous mixtures. Initially, the corresponding amount of alkanolamine, water and CO$_2$ molecules were randomly placed in a simulation box, which size was a bit larger than the nominal volumes for pure mixture components, and an energy minimisation was carried out. Then, an isothermal–isobaric (NPT) ensemble 2 ns simulation run (preceded by 500 ps of equilibration) was performed to define the solvent density and simulation box size for the next simulation stage. A Berendsen thermostat and barostat[21] with coupling parameters of 0.2 and 2 ps were used to maintain temperature and pressure. Then, a canonical (NVT) ensemble 20 ns simulation run (preceded by a 1 ns equilibration run) was carried out. A Nosé–Hoover thermostat[22], [23] with a coupling constant of 0.4 ps was used for temperature control. The equations of motion were integrated with a time step of 1.0 fs in both ensembles. Simulation trajectories were saved every 1 ps for further data analysis. CO$_2$ molecules were solvated at a concentration of about 0.2 M (0.1 M for DEAB cases) in aqueous alkanolamines which refers to typical experimental loadings. Simulations were carried out for alkanolamine/water solvent ratios of 7.5/92.5 (6/94 for the case of MEA), 30/70, 50/50, 80/20, and 100/0 (pure alkanolamine) (w/w) for the four molecule types. The amount of molecules and simulation box sizes for all studied molecular ensembles are provided in the ESI. Simulation box sizes were determined from preliminary simulations and checked for an absence of finite size effects.

The spatial distribution function (SDF) provides a 3-dimentional view of the preferred distribution of a molecule (or atom) around a reference molecule. The combination of one dimensional radial distribution functions (RDFs) with SDFs represents a very powerful tool of analysis to characterize and visualize solvent structure at the molecular level. SDFs of CO$_2$ around alkanolamines were performed with the TRAVIS package.[24] Diffusion coefficients were calculated from the mean square displacement and the observation time (over a 100–500 ps time interval). The residence autocorrelation
functions describe the probability of a CO₂ molecule to stay next to an alkanolamine molecule versus time and were calculated as described in[25]. As a criterion for a CO₂ molecule to be close to an alkanolamine molecule, a distance criterion which was obtained from the C_{alkanolamine}-C_{CO₂} RDF was used.

A distance between molecules was used as a criterion of a CO₂ molecule to reside next to an alkanolamine molecule. This distance in turn was extracted from C_{alkanolamine}-C_{CO₂} RDFs as the radial coordinate of the first minimum.

Results & discussion

Liquid densities of ternary CO₂/water/alkanolamine solutions and molecular conformations in solution

At the studied CO₂ concentrations of 0.1-0.2 M, the simulated liquid densities of alkanolamine/water/CO₂ ternary mixtures practically do not differ from those of the two component solvents (alkanolamine/water). [14] and in good agreement with experiment [26]

For example, for 30% (w/w) solutions of alkanolamine in water, the solution density only change by 0.1-0.2%, for example from 1019.7 kg m⁻³ to 1021.9 kg m⁻³ in the presence of CO₂ for MEA and from 973.0 to 979.8 kg m⁻³ for DEAB.

Table 1 Liquid densities (kg m⁻³) for binary alkanolamine/water and ternary alkanolamine/water/CO₂ mixtures at T=298 K.

| Composition | MEA MEA/W | MPA MPA/W | MMEA MMEA/W | DEAB DEAB/W |
|-------------|-----------|-----------|-------------|-------------|
| %wt of alkanolamines | MEA/W/CO₂ | MEA/W | MPA/W/CO₂ | MPA/W | MMEA/W/CO₂ | MMEA/W | DEAB/W/CO₂ | DEAB/W |
| 100 | 1037.4 | 1036.0 | 1011.3 | 1014.2 | 926.7 | 927.6 | 877.1 | 877.0 |
| 80 | 1043.8 | 1042.4 | 1024.3 | 1025.2 | 968.5 | 968.5 | 915.2 | 915.7 |
| 50 | 1033.5 | 1032.0 | 1022.6 | 1024.2 | 996.9 | 997.7 | 956.1 | 953.2 |
| 30 | 1021.9 | 1019.7 | 1013.2 | 1015.4 | 1000.9 | 1002.6 | 979.8 | 973.0 |
| 7.5 | 1005.4 | 1000.3 | 1002.7 | 1004.7 | 999.4 | 1002.0 | 996.8 | 997.8 |
In the ternary mixtures, the solution density increases by a less than 0.2% from that of the binary alkanolamine/water binary solution. This is in agreement with the atomistic modeling of CO$_2$ capture in primary and tertiary amines where a change of only a few percent of volume per amine molecule was observed even for high loadings of physisorbed carbon dioxide.[27]

Addition of carbon dioxide does neither affect the dominant molecular conformation of the alkanolamine molecules in solution. The alkanolamine and alkanolamine-water RDFs in the presence of CO$_2$ molecules are virtually identical to those of the binary solutions [14] and are not shown here. That is why we focus on characterizing the intermolecular interactions of carbon dioxide with alkanolamine and water molecules.

**Structural classification of ternary CO$_2$/water/alkanolamine solutions.**

Radial Distribution Functions (RDFs) are one-dimensional representations of an interatomic or intermolecular distance averaged over entire MD trajectories, e.g. they describe how close two particles of interest approach each other. The RDF function $g(ij, r)$ describes the relative probability of finding a pair of atoms $i$ and $j$ at the distance $r$ apart and relative to that of a uniform distribution at the same density. [28]

Figure 2 shows the RDFs of CO$_2$ with respect to solvent water (dotted lines) and the four alkanolamine molecules (solid lines) for a representative solution of 30/70 (w/w) of alkanolamine/water at T=313 K.
Figure 2 Liquid structures of ternary mixtures of CO$_2$/water/alkanolamine. RDFs of C$_{CO2}$-C$_{alkanolamines}$ (solid curves) and C$_{CO2}$-O$_W$ (dotted curves) for the 30/70 (w/w) of alkanolamine/water at T=313K. Blue, green, red and purples colours designate MEA, MPA, MMEA and DEAB accordingly.

For aqueous MEA, MPA and MMEA solutions, the peaks of the RDFs for CO$_2$-alkanolamines and CO$_2$-water are almost indistinguishable between the compounds (see Figure 2). This indicates that the water-CO$_2$ and alkanolamine-CO$_2$ interactions are very similar for the primary and secondary amines MEA, MPA and MMEA. The equal peak amplitudes for water and alkanolamines show that the CO$_2$ molecules are evenly distributed between the alkanolamine and water solvents and there is no preferred solvation. Also in the absence of CO$_2$, the binary solutions of the primary amines MEA, MPA and the secondary amine MMEA display identical RDFs. [14]

DEAB as a tertiary amine behaves differently. In water the DEAB molecules self-associate and start to form large hydrophobic clusters which here accomodate CO$_2$ molecules. The RDF peak amplitude for the carbon dioxide-DEAB interaction is significantly more pronounced than for CO$_2$-water (see Figure 2). This demonstrates a clear preference of CO$_2$ to stay in close vicinity of the DEAB molecules and clusters and avoid solvation by water molecules.

In the following, we are going to analyze in more detail the RDF for MPA at various concentrations. Since in that molecule the hydrophilic interactions with the hydroxyl and amine group are separated by three methyl groups, the discrimination between hydrophilic
and hydrophobic interactions is more distinct. The discussion also holds for the RDFs for MEA and MMEA which are given in the ESI.

**Localization of CO$_2$ molecules in aqueous MPA.**

Since aqueous MEA, MMEA and MPA solutions display very similar structural features in the presence of CO$_2$ (see above), only the results for MPA will be discussed here. The approach and association of solvated CO$_2$ molecules in aqueous MPA is characterized with the help of RDFs (Fig. 3), spatial distribution functions (SDFs) of CO$_2$ and water around MPA molecule (Fig. 4) and visualized by simulation snapshots (Fig. 5).
Figure 3 Further liquid structure details of the ternary mixture of CO\textsubscript{2}/water/alkanolamine. Results are shown here for MPA (for MEA and MMEA can be found in the ESI). Selected
RDFs between carbon dioxide and MPA and water at ratios of MPA/water (w/w) of 7.5/92.5 (orange curve), 30/70 (pink), 50/50 (cyan), 80/20 (magenta), and 100/0 (navy).

In aqueous MPA, the carbon dioxide molecules do not show any clear preference to as to approach the alkanolamine or water. This information follows from the fact that the amplitudes of the peaks of the RFDs of CO$_2$ interaction with MPA (Figure 3a) and water (Figure 3d) are of equal amplitude except for the 80/20 (w/w) MPA/water system (which we discuss in detail below). This was also reported for aqueous MEA solution.[15]

The broad peak at about $r = 0.49$ nm on the C$_{\text{MPA}}$-C$_{\text{CO}_2}$ curves (see Fig. 3a) originates from CO$_2$ molecules of the first solvation shell of MPA. One can discriminate between CO$_2$ alkanolamine interactions which are hydrophic in nature (with the carbon chain atoms (Figure 3a) and polar with the amine nitrogen (Figure 3b) and the hydroxyl group (Figure 3c).

The polar CO$_2$-MPA interactions (Figures 3b and 3c) decrease in RDF peak amplitude upon increase of water content since the carbon monoxide molecules are displaced by water which forms strong hydrogen bonds with the amine and hydroxyl groups of MPA. The exchange of CO$_2$ by water leads to a decrease of the effective first solvation shell radius from $r = 0.86$ nm to $r = 0.79$ nm.

The major five CO$_2$ orientations are displayed in Figure 4. Since the radial distribution function (RDF) is an orientation average over the angular coordinates, detail information of the local solution structure is lost. The spatial distribution function (SDF) [29] incorporates the radial and angular coordinates of the interatomic interactions and describes the three-dimensional density distribution of intermolecular interactions in a local coordinate system.
Figure 4 Preferred structural arrangements of CO$_2$ (green) and water (red) molecules with MPA. Projections of the spatial distribution functions (SDFs) of carbon atoms of carbon dioxide (green color) and oxygen atoms of water (red color) around MPA molecule for the 30/70 (w/w) MPA/water composition. Three carbon atoms of MPA were used to define 3D coordinate system. Iso-surfaces are drawn at density level of 50%. Five main localizations of carbon dioxide around MPA molecule are numbered (see text). Water molecules are located mainly in three distinct regions (determined by locations of hydrogen atoms) around each polar groups of MPA.

Region 1 in Figure is the dominant location of CO$_2$ in the vicinity of MPA. It refers to the hydrophobic interaction of CO$_2$ with the carbon chain methyl groups of MPA in an orientation quasi-parallel to the MPA molecule (see Fig. 5a).
As to the polar interactions between CO$_2$ and MPA, three types can be distinguished from Figures 3b and c and Figure 4.

- A direct interaction of the N$_{\text{MPA}}$ and C$_{\text{CO2}}$ atoms occurs very rarely and can only be seen as a small shoulder in the RDF (Figure 3b) at $r = 0.32$ nm. This is due to the two hydrogens of the amine group NH$_2$ which hinder a closer approach of CO$_2$ towards the nitrogen atom.

- The SDF regions 2 and 4 in Figure 4 are instances in which the O atoms of carbon dioxide act as hydrogen bond acceptors of the NH$_2$ group protons (see Figure 5b). This is the large peak at $r = 0.41$ nm in Figure 3b.

- One of the most frequent molecule arrangements is visualized in Figure 5c. The shoulder of the RDFs at $r = 0.55$ nm (Figure 3c) is composed of CO$_2$ molecules.
acting as hydrogen bond acceptors of the hydroxyl group of MPA. The same information can also be obtained from an analysis of the HO\textsubscript{MPA}-C\textsubscript{CO2} RDFs.

Upon increase of the water content, the water molecules displace CO\textsubscript{2} molecules from positions close to the O\textsubscript{MPA}, N\textsubscript{MPA} atoms, the respective peaks in the RDF decrease in amplitude and the interaction radius increases to r = 0.41 nm (Figure 3c) whereas the first solvation shell decreases in radius (Figure 4, red areas). A snapshot can be seen in Figure 5d.

The aqueous solvation of carbon dioxide (Figure 3d) gives an intermolecular distance of r = 0.40 nm between the C\textsubscript{CO2}-O\textsubscript{w} atoms for the first solvation shell. At 80/20 (w/w) MPA/water, the amplitude for that radial coordinate significantly decreases, also the first minimum of the RDF (at r=0.33 nm) becomes smaller and broader. At this mixture composition, the MPA/water phase separation sets in and the water molecules are organized in small isolated clusters which was also observed for MEA [15] Carbon dioxide is not included in these clusters but interacts with a few separate water molecules in the vicinity of the polar groups of MPA.

The same line of argumentation also holds for ternary mixtures of the MEA and MMEA alkanolamine compounds (see ESI).

**Localization of CO\textsubscript{2} molecules in aqueous DEAB solution.**

The behaviour of carbon dioxide in aqueous solutions of DEAB is significantly different from that in MEA, MMEA and MPA. Figures 6, 7 and 8 give structural information about the preferred intermolecular distances, localization of approaching CO\textsubscript{2} and relative orientations in solution of water and DEAB.
Figure 6 Complex liquid structure of ternary mixtures of CO$_2$/water/DEAB at different solvent compositions. The RDFs of intermolecular interactions of carbon dioxide, DEAB
and water at ratios of DEAB/water (w/w) of 7.5/92.5 (orange curve), 30/70 (pink), 50/50 (cyan), 80/20 (magenta), and 100/0 (navy).

Whereas CO₂ interactions with primary and secondary amines were equally distributed between water and the absorbent, the RDFs of CO₂ molecules in aqueous DEAB at various DEAB concentrations (Figure 6 a-c) show that carbon dioxide molecules are preferrably located in close vicinity to DEAB molecules and avoid water. The amplitude of the RDF for CO₂–water (Figure 6d) is lower than for all CO₂-DEAB interactions (Figure 6 a-c). Second, the peaks for CO₂-water are less than 1, meaning that the probability of interactions for the CO₂-water pair is less likely than expected just on their nominal composition. At increasing water concentration, this preference becomes stronger which can be seen in the increase of the CO₂-DEAB peak amplitude. The CO₂-DEAB RDF peaks increase until 30/70 (w/w) DEAB/water, and then decrease at higher water content. This effect is also seen for the intermolecular DEAB-DEAB interactions and shows that.[14] The distribution of CO₂ around DEAB molecules is independent of the amount of water in solution, except for the 7.5/92.5 (w/w) DEAB/water mixture.
Figure 7 Structural mapping of the first solvation shell carbon dioxide (green) and water (red) with DEAB. The spatial distribution functions (SDFs) of carbon atoms of CO$_2$ and oxygen atoms of water around DEAB molecule for the 30/70 (w/w) DEAB/water composition. Three carbon atoms of DEAB adjoining the N atom were used to define 3D coordinate system. Iso-surfaces are drawn at 50%. The major five locations of carbon dioxide around the DEAB molecule are numbered (see text). Water molecules show only two main locations - next to nitrogen atom.
Solvent water molecules show two main locations close to the amine nitrogen atom with which they form hydrogen bonds. On average, each nitrogen atom of DEAB molecule forms about 0.97 hydrogen bonds with water at 7.5/92.5 (w/w). [14]

From the SDFs (Figure 7), we can identify several sites of interaction between CO$_2$ and the DEAB.

- First, the peak at a distance of 0.47 nm in the C$_{DEAB}$-C$_{CO2}$ RDF (Figure 6a) reflects the hydrophobic interactions with the 2-butanol chain of DEAB (see locations 5 and 6 in Figure 7 and the snapshot in Figure 8a). The CO$_2$ molecules tend to arrange perpendicular to the 2-butanol chain due to steric interactions with the diethylamine groups (see ESI).

- The second peak at r=0.62 nm refers to CO$_2$ molecules interacting with the ethyl groups of DEAB (regions 3 and 4 in Fig. 7 and the snapshot in Fig 8b).
• The second CO2 solvation shell at r=1.1 nm is almost invariant from a change in composition, unlike in the MPA case. This suggests that CO2 molecules stay close to the DEAB clusters and their distances do not change.

• The N_{DEAB}-C_{CO2} RDF reveals a first small peak at r=0.33 nm which are CO2 molecules approaching the N_{DEAB} atom (regions 1 and 2 in Fig. 7, and the snapshot in Fig. 8c). These are spatially confined regions of approach and that is why they appear clearly visible in Figure 7. At a 7.5/92.5 composition this peak is vanishes since water molecules displace the CO2 molecules from interactions with the N atom and form a strong hydrogen bond network with other water molecules in surrounding DEAB (the DEAB fraction is only 1% molar).

• The large broad peak at r= 0.55 nm is created by CO2 molecules interacting with hydrophobic chains of DEAB and corresponds to regions 3-6. The peaks at r=1.0 nm correspond to the second solvation shell of DEAB by CO2.

• A direct interaction between CO2 and the alkanolamine DEAB is to be seen from the first peak at r=0.31 nm of the C_{CO2}-O_{DEAB} RDF (snapshot in Fig. 8d). This interaction decreases upon addition of water since the water molecules are competing as solvent. At 7.5/92.5 (w/w) DEAB/water, CO2 molecules start interacting with the water molecules around the OH group of DEAB.

The RDFs for water-CO2 (Fig. 6d) corroborate the preference of CO2 staying in close vicinity of the DEAB clusters and avoiding wate. The peak amplitudes of first peak are below than 1 for all compositions, except for the 7.5/92.5 (w/w) DEAB/water. The decrease in amplitude at r=1 nm with increasing water concentration (for 80/20, 50/50 and 30/70 (w/w) DEAB/water), is a clear evidence of the self-clustering of DEAB molecules and an incorporation of CO2 molecules.
The dynamics of CO$_2$ in aqueous alkanolamine solutions.

Diffusion coefficients are macroscopic characteristics of the microscopic molecular mobility in a solvent. Molecular diffusion coefficients are very important parameters in the engineering, simulation and optimization of chemical processes. The diffusion coefficients of CO$_2$ in different alkanolamine/water solutions, however, are experimentally not accessible due to the spontaneous chemical reactivity of the molecule with the amine. That is why all published CO$_2$ diffusion data in alkanolamines are only estimates and derived from N$_2$O mobility analysis. There is recent evidence that the use of the ratio of the solubility of N$_2$O to that of CO$_2$ in water may be restricted to dilute systems only. The use of the CO$_2$/N$_2$O data extraction requires reliable experimental Henry constants of CO$_2$ and N$_2$O in water. There is a remarkable lack of VLE data on the N$_2$O–water system in literature which prompted the computation of CO$_2$ diffusion coefficient in complex mixtures.

CO$_2$ diffusion coefficients in aqueous alkanoamine solution can be obtained from the velocity autocorrelation function in MD simulations. In Figure 9, the simulated CO$_2$ diffusion coefficients of MEA and DEAB are compared with experiment estimates from N$_2$O diffusion measurements.[30][31][32][33]. The computed diffusion coefficients are in excellent agreement with available experimental N$_2$O diffusion data rescaled to CO$_2$ between 298-323 K and for 30% and 50% alkanolamine solutions, which shows the accuracy of our computational approach. Apparently, for these mixture compositions the use of rescaled N2O diffusion coefficients seems appropriate. The values for all alkanolamine molecules are given in the ESI.
Figure 9 Comparison of experimental and simulated diffusion coefficients of carbon dioxide in aqueous alkanolamines. Black symbols (triangles, squares, semi-filled circles and diamonds) are experimental data derived from nitrous oxide diffusion[30][31][32][33]. Blue and purple semi-filled circles are computed diffusion coefficients for aqueous 70/30 (w/w) MEA and DEAB solutions, respectively. Percentage numbers denote the weight fraction composition of alkanolamines in water.

Figure 10 shows the CO\textsubscript{2} diffusion coefficients for all alkanolamine solutions over a wide range from 7.5 to 100\% of all studied mixture compositions and in a temperature range from 298 to 323 K. For all aqueous alkanolamine solutions, the diffusion coefficients increase with temperature. The diffusion of CO\textsubscript{2} increases in the following order MEA > MPA = MMEA > DEAB for water-rich compositions. For dilute solutions of 7.5 and 30\%, the diffusion coefficient increases linearly with temperature. As the alkanolamine fraction increases, the carbon dioxide diffusion is slower due to steric hindrance and an increase in solvent density. The higher the , the slower the CO\textsubscript{2} diffusion in solution. Above 50\%, the temperature-dependence deviates from linearity which and the system deviates from ideal behaviour.[10] The same effect is also observed for the diffusion the alkanolamine molecules in water.
Figure 10 Simulated temperature dependence of diffusion coefficients of carbon dioxide in aqueous alkanolamine solutions at various mixture compositions: MEA (blue color), MPA (green), MMEA (red), and DEAB (purple). Percentage numbers denote weight fraction of alkanolamines in water. The values can be found in the ESI.

A compound-specific comparison of the mixture-dependent CO$_2$ diffusion can be seen in Figure 11. For low alkanolamine concentrations, the CO$_2$ diffusion correlates with
the molecular size: it is fastest in MEA, MPA and MMEA and slow in DEAB. The ordering of alkanolamine compounds for CO$_2$ diffusion in changes for alkanolamine-rich solution. For pure MMEA solutions the liquid density noticeably decreases by 15%, the ability to form hydrogen bonds is less than for MEA and MPA molecules and then the CO$_2$ diffusion in solution becomes faster and exhibits the largest diffusion coefficient. [14]

![Graph of simulated diffusion coefficients of carbon dioxide in aqueous alkanolamines versus mixture compositions at T= 313 K. Color codes are analogous to Figure 10.](image)

*Figure 11* Simulated diffusion coefficients of carbon dioxide in aqueous alkanolamines versus mixture compositions at T= 313 K. Color codes are analogous to Figure 10.

Also for DEAB concentrations higher than 80/20 w/w CO$_2$diffuses faster than in MEA and MPA solutions at identical compositions. This enhanced CO$_2$ diffusion can be attributed to the above discussed localization of CO$_2$ in hydrophobic DEAB clusters and not in water. For these amine-rich compositions, CO$_2$ is to be found in the hydrophobic environment of large tertiary amines in which it diffuses fast.

**Kinetic Aspects of CO$_2$ Interaction with Alkanolamines in Solution**

The average residence time of CO$_2$ molecules to stay close to alkanolamine molecules to characterize the kinetics of CO$_2$-alkanolamine interactions in solution was calculated. As a distance criterion, the radius of the first solvation shell from the RDF was used.

The residence autocorrelation functions (see ESI) of the four studied molecules reveal two components (see Figure 12). The long residence is in the range of 5-20 ps and another shorter one in the range of 0.5-1 ps. The long residence component corresponds
to direct hydrophobic interaction of CO$_2$ with the alkanolamine molecules (the alky -CH$_2$- chain) and the short residence time is related to interactions between the nitrogen atoms of the alkanolamine and the carbon atoms of CO$_2$.

![Graph showing residence times of CO$_2$ molecules located next to alkanolamine molecules at T= 313 K. Color-codes are analogous to Figure 10.](image)

These residence times generally follow the same trend as the diffusion coefficients in Figure 10.

**Table 2** Calculated two-component residence times (slow (hydrophobic) and fast (polar) components, in ps) of CO$_2$ molecule located next to alkanolamine molecules in aqueous solution at T= 313 K. (*) For MEA case this composition is 0 and the value corresponds to water then.

| Composition %wt of alkanolamines | MEA | MPA | MMEA | DEAB |
|-------------------------------|-----|-----|------|------|
|                               | fast | slow | fast | slow | fast | slow | fast | slow |
| 100                           | 0.90 | 11.30 | 1.03 | 19.23 | 0.90 | 9.81 | 1.04 | 17.33 |
| 80                            | 0.88 | 10.95 | 0.93 | 15.39 | 0.95 | 12.56 | 1.03 | 20.15 |
| 50                            | 0.75 | 7.63  | 0.87 | 11.24 | 0.84 | 11.27 | 1.13 | 21.25 |
| 30                            | 0.68 | 6.17  | 0.76 | 8.73  | 0.78 | 10.36 | 1.07 | 18.00 |
| 7.5                           | 0.66$^{*}$ | 4.94$^{*}$ | 0.61 | 7.00  | 0.63 | 8.53 | 0.93 | 15.63 |

The shortest residence time of CO$_2$ is seen for the MEA molecule (0.6 ps and 6 ps) which also displays the fastest CO$_2$ diffusion. The longest residence (0.9-1.0 and 15-18 ps)
and the slowest CO$_2$ diffusion is observed for DEAB. As the alkanolamine concentration increases, the average residence times become longer since the CO$_2$ diffusion slows down. For pure MMEA the residence time decreases because of the above mentioned decrease of MMEA density and its lower ability to create hydrogen bonds. For DEAB the residence times decrease from the 50/50 composition on. The CO$_2$ molecules reside in DEAB clusters and move faster in that hydrophobic environment. With increase of DEAB concentration, the water-free hydrophobic regions become larger and lead to shorter residence times.

**Conclusion**

Chemical absorptive removal of CO$_2$ from biogas to fulfil pipeline specifications requires novel and more efficient CO$_2$-absorbing molecules. Besides thermodynamic properties such as low heat of absorption and ease of solvent recovery, a more comprehensive set of parameters must also be considered related to liquid structure properties such as solubility, diffusion, non-ideality and kinetic aspects. Computer-aided molecule design can provide some of these data which are difficult to obtain or inaccessible by experiment.

Solvent structural details of CO$_2$ dissolved in aqueous alkanolamine solution of scrubbing compounds with different properties (MEA, MPA, MMEA and DEAB) were obtained over a large range of ternary mixture compositions and a temperature range between 298 – 323 K. Solvent densities, CO$_2$ diffusion properties and the molecular structure of the complex ternary mixtures can be obtained from molecular simulations but are not available from experiment. The liquid solution densities and the liquid state structure of these ternary mixtures, the most important CO$_2$-alkanolamine interactions in solutions and the diffusion coefficient of CO$_2$ molecules could be obtained.

CO$_2$ absorption is a balance between aqueous solvation and desolvation, hydrogen bonding and hydrophobic interactions and very sensitive to the exact composition of the solution. In aqueous solutions of MEA, MMEA and MPA, the solvation and distribution of carbon dioxide is very similar and the solute shows no preferrential interaction with either water or the alkanolamine. At a composition of 80/20 w/w alkanolamine/water, water tends to form large clusters void of CO$_2$. At increasing of water concentration, the water molecules are forming hydrogen bonding interactions with the hydroxyl and amine groups of the alkanolamines and are displacing CO$_2$. This shows that at low alkanolamine
concentrations CO₂ diffusion and approach is fast and easy for primary and secondary amines but at higher amine loadings hydrophilic interactions with solvent water are obstructing the direct reaction with CO₂.

In aqueous DEAB solutions, however, the solute CO₂ molecules are preferrably located inside large clusters of self-associated DEAB molecules with a long residence time. Already at 7.5/92.5 w/w DEAB/water ration, two DEAB molecules associate and are connected by a water-mediated hydrogen bond network. As a tertiary amine, it does not directly react carbon dioxide but rather acts as a base which then catalyzes the hydration of CO₂.[34] DEAB (4-diethylamino-2-butanol) was specifically designed as a molecule with high CO₂[35] and predicted to have a lower degree of toxicity than MEA.

The lack of accurate parameters for alkanolamines in solution is due to experimental difficulties at high loadings and the need for proper vapor-liquid equilibrium (VLE) model.

The overall process simulation and optimization of new CO₂ sequestration procedures, however, require detailed thermodynamic and kinetic properties of the ternary solutions of CO₂/water/alkanolamine as simulation parameters. For novel compounds, liquid structure data such as solvent densities, optimal alkanolamine/water ratio and dynamic properties such as diffusion coefficients, CO₂-accessibility and residence time are not available experimentally but accessible by MD simulations. In particular, as the chemical nature of the absorbing molecule changes, significantly different properties can be noted. Computer-aided molecular engineering can here assist the design of novel and highly efficient compounds for absorptive CO₂ removal from biogas.

Conflicts of interest

The authors declare no conflict of interest.

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References

1. Raupach MR, Marland G, Ciais P, Le Quéré C, Canadell JG, Klepper G, et al. Global and regional drivers of accelerating CO<sub>2</sub> emissions. Proceedings of the National Academy of Sciences [Internet]. 2007 Jun 12;104(24):10288. Available from: https://doi.org/10.1073/pnas.0700609104

2. G. Speight J. Handbook of Natural Gas Analysis [Internet]. 2018. Available from: https://doi.org/10.1002/978111919240297

3. Chen X, Vinh H, Avalos Ramirez A, Rodrigue D, Kaliaguine S. Membrane gas separation technologies for biogas upgrading [Internet]. 2015. (RSC Adv.; vol. 5). Available from: https://doi.org/10.1039/C5RA00666J

4. Rochelle GT. Amine Scrubbing for CO\2\ Capture. Science [Internet]. 2009;325(5948):1652–4. Available from: http://science.sciencemag.org/content/325/5948/1652.abstract

5. Dutcher B, Fan M, Russell AG. Amine-based CO2 capture technology development from the beginning of 2013-A review. ACS Appl Mater Interfaces [Internet]. 2015;7:2137–48. Available from: https://doi.org/10.1021/am507465f

6. D’Alessandro DM, Smit B, Long JR. Carbon Dioxide Capture: Prospects for New Materials. Angew Chem, Inter Ed [Internet]. 2010;49(35):6058–82. Available from: https://doi.org/10.1002/anie.201000431

7. Stowe HM, Hwang GS. Fundamental Understanding of CO2 Capture and Regeneration in Aqueous Amines from First-Principles Studies: Recent Progress and Remaining Challenges. Ind Eng Chem Res. 2017;56:6887–6899.

8. Yang X, Rees RJ, Conway W, Puxty G, Yang Q, Winkler DA. Computational Modeling and Simulation of CO 2 Capture by Aqueous Amines. Chem Rev [Internet]. 2017;117:9524–9593-9524–9593. Available from: https://doi.org/10.1021/acs.chemrev.6b00662
9. Papadopoulos Al, Badr S, Chremos A, Forte E, Zarogiannis T, Seferlis P, et al. Computer-aided molecular design and selection of CO2 capture solvents based on thermodynamics, reactivity and sustainability. Mol Syst Des Eng [Internet]. 2016;1:313–34. Available from: https://doi.org/10.1039/C6ME00049E

10. Monteiro JGM-S, Svendsen HF. The N2O analogy in the CO2 capture context: Literature review and thermodynamic modelling considerations. Chemical Engineering Science [Internet]. 2015 Apr 14;126:455–70. Available from: http://www.sciencedirect.com/science/article/pii/S0009250914007416

11. Chen Q, Balaji SP, Ramdin M, Gutiérrez-Sevillano JJ, Bardow A, Goetheer E, et al. Validation of the CO2/N2O analogy using molecular simulation. Ind Eng Chem Res [Internet]. 2014;53:18081–90. Available from: https://doi.org/10.1021/ie503488n

12. Stowe HM, Vičiauskas L, Paek E, Hwang GS. On the origin of preferred bicarbonate production from carbon dioxide (CO2) capture in aqueous 2-amino-2-methyl-1-propanol (AMP). Phys Chem Chem Phys. 2015;17:29184–92.

13. Narimani M, Amjad-Iranagh S, Modarress H. Performance of tertiary amines as the absorbents for CO2 capture: Quantum mechanics and molecular dynamics studies. Journal of Natural Gas Science and Engineering [Internet]. 2017 Nov 1;47:154–66. Available from: http://www.sciencedirect.com/science/article/pii/S1875510017303827

14. Melnikov SM, Stein M. Molecular Dynamics Study of the Solution Structure, Clustering, and Diffusion of Four Aqueous Alkanolamines. J Phys Chem B [Internet]. 2018;122(10):2769–78. Available from: https://doi.org/10.1021/acs.jpcb.7b10322

15. Da Silva EF, Kuznetsova T, Kvamme B, Merz Jr KM. Molecular dynamics study of ethanolamine as a pure liquid and in aqueous solution. J Phys Chem B [Internet]. 2007;111:3695–703. Available from: https://doi.org/10.1021/jp068227p

16. Huang IS, Li JJ, Tsai MK. Solvation dynamics of CO2(g) by monoethanolamine at the gas-liquid interface: A molecular mechanics approach. Molecules [Internet]. 2017;22:8–8. Available from: https://doi.org/10.3390/molecules22010008

17. Jorgensen WL, Maxwell DS, Tirado-Rives J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. J Am Chem Soc [Internet]. 1996;118:11225–11236-11225–11236. Available from: https://doi.org/10.1021/ja9621760
18. Berendsen HJC, Grigera JR, Straatsma TP. The missing term in effective pair potentials. J Phys Chem [Internet]. 1987;91:6269–6271. Available from: https://doi.org/10.1021/j100308a038

19. J.J. Potoff JIS. Vapor-Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen. AIChE J. 2001;47:1676–1682.

20. Abraham MJ, Murtola T, Schulz R, Páll S, Smith JC, Hess B, et al. Gromacs: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. SoftwareX [Internet]. 2015;1–2:19–25. Available from: https://doi.org/10.1016/j.softx.2015.06.001

21. H.J.C. Berendsen WF van G JPM Postma. Molecular-Dynamics with Coupling to an External Bath. J Chem Phys. 1984;81:3684–3690.

22. Nosé S. A unified formulation of the constant temperature molecular dynamics methods. J Chem Phys [Internet]. 1984;81:511–511–511–519. Available from: https://doi.org/10.1063/1.447334

23. Hoover WG. Canonical dynamics: Equilibrium phase-space distributions. Phys Rev A [Internet]. 1985;31:1695–1697-1695–1697. Available from: https://doi.org/10.1103/PhysRevA.31.1695

24. Brehm M, Kirchner B. TRAVIS - A free analyzer and visualizer for monte carlo and molecular dynamics trajectories. J Chem Inf Model [Internet]. 2011;51:2007–23. Available from: https://doi.org/10.1021/ci200217w

25. Melnikov SM, Höltzel A, Seidel-Morgenstern A, Tallarek U. A Molecular Dynamics View on Hydrophilic Interaction Chromatography with Polar-Bonded Phases: Properties of the Water-Rich Layer at a Silica Surface Modified with Diol-Functionalized Alkyl Chains. J Phys Chem C [Internet]. 2016;120(24):13126–13138-13126–13138. Available from: https://doi.org/10.1021/acs.jpcc.6b03799

26. Weiland RH, Dingman JC, Cronin DB, Browning GJ. Density and Viscosity of Some Partially Carbonated Aqueous Alkanolamine Solutions and Their Blends. Journal of Chemical & Engineering Data [Internet]. 1998 May 1;43(3):378–82. Available from: https://doi.org/10.1021/je9702044

27. Maiti A, Bourcier WL, Aines RD. Atomistic modeling of CO2 capture in primary and tertiary amines - Heat of absorption and density changes. Chem Phys Lett. 2011;509:25–8.
28. Frenkel D, Smit B. Understanding molecular simulation: from algorithms to applications. San Diego; 2002.

29. Kusalik PG, Svishchev IM. The spatial structure in liquid water. Science [Internet]. 1994;265(5176):1219–21. Available from: https://doi.org/10.1126/science.265.5176.1219

30. Ying J, Eimer DA. Measurements and correlations of diffusivities of nitrous oxide and carbon dioxide in monoethanolamine + water by laminar liquid jet. Ind Eng Chem Res. 2012;51:16517−16524.

31. Li M-H, Lai MD. Solubility and Diffusivity of N2O and CO2 in (Monoethanolamine + N-Methyldiethanolamine + Water) and in (Monoethanolamine + 2-Amino-2-methyl-1-propanol + Water). J Chem Eng Data. 1995;40:486–92.

32. Mandal BP, Kundu M, Bandyopadhyay SS. Physical Solubility and Diffusivity of N2O and CO2 into Aqueous Solutions of (2-Amino-2-methyl-1-propanol + Monoethanolamine) and (N-Methyldiethanolamine + Monoethanolamine). J Chem Eng Data. 2005;50:352–8.

33. Sema T, Edali M, Naami A, Idem R, Tontiwachwuthikul P. Solubility and diffusivity of N2O in aqueous 4-(diethylamino)-2-butanol solutions for use in postcombustion CO2 capture. Ind Eng Chem Res. 2012;51:925–30.

34. Shi H, Sema T, Naami A, Liang Z, Idem R, Tontiwachwuthikul P. 13C NMR Spectroscopy of a Novel Amine Species in the DEAB–CO2–H2O system: VLE Model. Industrial & Engineering Chemistry Research [Internet]. 2012 Jun 27;51(25):8608–15. Available from: https://doi.org/10.1021/ie300358c

35. Maneeintr K, Idem RO, Tontiwachwuthikul P, Wee AGH. Synthesis, solubilities, and cyclic capacities of amino alcohols for CO2 capture from flue gas streams. In 2009. p. 1327–34. Available from: https://doi.org/10.1016/j.egypro.2009.01.174