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CO_2 Capture in Amine Solutions: Modelling and Simulations with Non-Empirical Methods

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Absorption in aqueous amine solutions is the most advanced technology for the capture of CO2, although suffering from drawbacks that do not allow exploitation on large scale. Search for optimum solvents has been pursued with empirical methods and has also motivated a number of computational approaches over the last decade. However, a deeper level of understanding of the relevant chemical reactions in solution is required so as to contribute to this effort. We present here a brief critical overview of the most recent applications of computer simulations using ab initio methods. Comparison of their outcome shows a strong dependence on the structural models employed to represent the molecular systems in solution and on the strategy used to simulate the reactions. In particular, the results of very recent ab initio molecular dynamics augmented with metadynamics are summarized, showing the crucial role of water, which has been so far strongly underestimated both in the calculations and in the interpretation of experimental data. Indications are given for advances in computational approaches that are necessary if meant to contribute to the rational design of new solvents.

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Abstract

Absorption in aqueous amine solutions is the most advanced technology for the capture of CO_2, although suffering from drawbacks that do not allow exploitation on large scale. Search for optimum solvents has been pursued with empirical methods and has also motivated a number of computational approaches over the last decade. However, a deeper level of understanding of the relevant chemical reactions in solution is required so as to contribute to this effort. We present here a brief critical overview of the most recent applications of computer simulations using *ab initio* methods. Comparison of their outcome shows a strong dependence on the structural models employed to represent the molecular systems in solution and on the strategy used to simulate the reactions. In particular, the results of very recent *ab initio* molecular dynamics augmented with metadynamics are summarized, showing the crucial role of water, which has been so far strongly underestimated both in the calculations and in the interpretation of experimental data. Indications are given for advances in compu-

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1 Introduction

The disastrous impact of anthropogenic carbon dioxide (CO_2) emissions on the environment is one of the main concerns of our era. Among the options under examination for the reduction of these emissions and the mitigation of global climate change, capture and sequestration of CO_2 from fossil fuel combustion is considered one of key importance for a viable and near-term solution.

Amine aqueous solutions were first proposed back in 1930[1] as chemical absorbents for the separation and removal of CO_2 from gas mixtures, via a cyclic process in which CO_2 is selectively and reversibly absorbed. Indeed, amine scrubbing has long been used in the chemical industry for removal from gas streams, but only at the beginning of the '90's it started to be evaluated for CO_2 capture from fossil-fuel-fired power plants. In spite of serious - and repeatedly expressed - concerns about the excessive cost of the operation, amine solutions are still at the heart of the most mature post-combustion capture technology.[2–6] Monoethanolamine (MEA) is the most extensively employed amine, primarily because of its high reactivity to CO_2, relative low solvent cost, and special ease of reclamation.[7] However, the use of MEA suffers from several drawbacks, including a relatively low CO_2 loading capacity, relatively easy oxidative degradation - leading to amine loss and apparatus corrosion[8–10] - and high regeneration energy (see, e.g., Ref. 11). These disadvantages are only partially alleviated by the introduction of a blending amine such as piperazine.[12–15] Improvement of the available solvents, search for novel candidates and process optimization are the targets of ongoing research, which is mainly based on experimental methods.[16–20]

Building fundamental knowledge is necessary for the rational design of alternative solvents. Although the intrinsic complexity of the systems to be investigated does not allow for a comprehensive approach and indeed limits the validity of any reduction procedure, some basic questions can - and should - still be addressed. In particular, we refer to the key chemical reactions, their mechanisms and the factors that influence their rates. Beyond the great experimental effort aimed at this understanding, atomistic simulations and quantum-chemical calculations - started with the seminal papers by daSilva, Stevenson and collaborators[21,22] - have grown over the years.[23–38]

By providing a critical survey of the recent computational studies, this paper is intended to contribute to clarify key questions related to the microscopic mechanisms accompanying the absorption of CO_2. In particular, we shall concentrate on primary amines, and especially MEA and the uptake of CO_2, which have been the focus of theoretical research, and examine to what extent the results depend on the model and method adopted. Indeed, traditional quantum-chemical calculations have strongly underestimated the role of water, which, on the contrary, has emerged as crucial from recent *ab initio* studies of the dynamics of several chemical reactions in solution.[28,32,33] We shall report on the latter in more detail, and also on their extension to 2-amino-2-methyl-1,3-propanediol (AMPD),[38] whose structure can be considered as derived from that of MEA after a double substitution, with a methyl and a hydroxymethyl group. The molecular structures are illustrated in Figure 1.

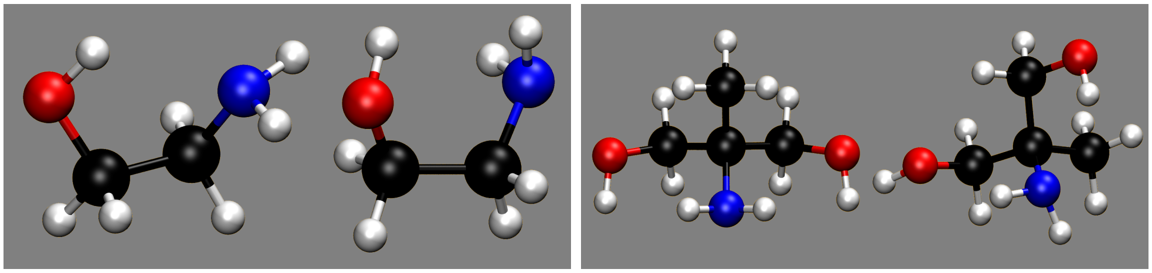

Figure 1: MEA (left) and AMPD (right) conformers

1.1 Relevant chemical reactions

Amines are organic derivatives of ammonia (NH_3), in which one, two, or all three hydrogens are replaced by organic (R) groups; according to the number of substituted hydrogens, one designates them as primary (RNH_2), secondary (R_1R_2NH) or tertiary ($R_1R_2R_3N$) amines. In analogy with their parent molecule, the unshared pair of electrons at the (sp^3 hybridized) nitrogen atom makes amines bases and nucleophiles. In particular, their basicity is stronger than that of water. For example, the acidity constant pK_a is 9.26 for NH_3 and for primary amines of interest here, MEA ($R{=}CH_2CH_2OH$), 2-amino-2-methyl-1,3-propanediol (AMPD) ($R{=}C(CH_2OH)_2CH_3$) and 2-Amino-2-methyl-1-propanol (AMP) ($R{=}C(CH_2OH)(CH_3)_2$), pK_a (25°C) = 9.45, 8.72 and 9.82 respectively.[39]

The reaction of solvated CO_2 with primary amines in aqueous solution can be expressed as

$$CO_2 + 2RNH_2 \rightleftharpoons RNHCOO^- + RNH_3^+ \ (1).$$

where $RNHCOO^-$ represents the carbamate (anion) and RNH_3^+ is a protonated amine.

Carbamates dominate the reaction products in the case of several primary and secondary amines, like MEA,[40] and are accompanied by protonated amines.[20,41] On the contrary, sterically-hindered amines,[42] like AMP, are unlikely to form carbamates[18,43–45] and mainly generate bicarbonates. The formation of carbamates is associated with fast kinetics but the need of two amines per CO_2 limits the loading capacity, and amine regeneration from the reverse route requires a high energy penalty. CO_2 uptake into bicarbonate is much slower but does not require an additional amine and thus provides higher loading capacity to the solution. Moreover, amine regeneration is less expensive. However, the role of the amine remains unclear, namely, as proton acceptor, it can merely promote water splitting or also act as catalyst for the binding of a hydroxide to CO_2.

Several observations and the associated kinetic models[46,47] have lead to propose that reaction (1) develops via two sequential steps, namely the formation of a zwitterion ($RNH_2^+COO^-$):

$$CO_2 + RNH_2 \rightleftharpoons RNH_2^+COO^- \ (2a)$$

and its deprotonation:

$$RNH_2^+COO^- + B \rightleftharpoons RNHCOO^- + BH^+ \text{ (2b)},$$

where B is any of the bases present in the solution, namely another amine, a water molecule or a hydroxide. As mentioned above, the ultimate product contains protonated amines ($B{=}RNH_2$.)

However, it is well known that the zwitterion eludes direct observation. This situation has raised doubts on its relevance and has often lead to suggest an alternative mechanism that involves carbamic acid (RNHCOOH) as intermediate (see, e.g., Ref. 16):

$$CO_2 + RNH_2 \rightleftharpoons RNHCOOH \text{ (3a)}$$

and its deprotonation

$$RNHCOOH + B \rightleftharpoons RNHCOO^- + BH^+ \text{ (3b)}.$$

No experimental data confirm this role of the carbamic acid, although its hydrolysis is expected to be less probable than that of the zwitterion. ^{1}H NMR measurements of chemical shifts and protonation constants in acidic aqueous solutions containing MEA and MEA-carbamate were interpreted as sign of the presence of carbamic acid.[40]

Both carbamate formation and amine regeneration are activated processes. In particular, reaction rates measurements - over a temperature range of 298 K to 313 K - were interpreted according to (2a)-forward and provided an estimate of ∼11kcal/mol for the activation energy of the zwitterion formation.[47]

Therefore, a knowledge-driven search for improvement should care about establishing the factors that influence the rate of all relevant reactions. As a consequence, understanding the microscopic mechanisms and their relative probability is also the primary concern of any type of modelling and simulation at the atomistic level.

1.2 The computational approach

Starting from the work by da Silva, Svendsen and collaborators,[21] quantum-chemical computations aimed at understanding whether and how the carbamate would form from the interaction between a CO_2 and an amine molecule in solution, have followed a similar protocol, consisting of geometry optimization for the reactant and product species and pre-arranged (intermediate) complexes as well as search for transition states (TS). Many are however the distinct characteristics: the size of the model systems, namely the number of molecules included, the representation of water, namely either implicit or partially explicit, the level of theory, ranging from Hartree-Fock[21] to Density Functional Theory (DFT) and the latter with different exchange-correlation functionals, the specific computational scheme, e.g., the type of localized basis functions, and - if appropriate - the TS search strategy. Some are summarized in Table 1. [1].

DFT-based molecular dynamics (MD) has also started to be used as complementary to the traditional strategy, namely mainly as a guiding tool to obtain further insights into possible configurations of the amines and their derivatives in explicit water, and into probable processes leading to carbamates. Table 1 reports the distinct features of these simulations. However, given the strong time limitation, the results of unbiased DFT-MD can hardly provide information on activated processes.

More extensive studies of the dynamics of reactions (2) and (3) have recently been carried out, also based on DFT-MD but aided by metadynamics (MTD)[48] to enhance the sampling of the configurational space. For each reaction, probable paths were thus established, also unforeseen, free-energy profiles were reconstructed and in particular an estimate of the corresponding free-energy barriers (FEBs; ΔF^*) were obtained.[28,32,33,38] We emphasize that, in contrast with most of the calculations mentioned above, no constraint was applied in this protocol, such as to guide the reaction towards a given product or along a given pathway. This advantage will become clear in the account of the results below.

Metadynamics was applied with simple collective variables, namely the N-H distance for deprotonation and the N-C distance for CO_2 release. Analogous results were obtained when using (local) coordination numbers, as shown in Ref. 28. A more stringent veri-

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[1] In some cases, DFT-based geometry optimization in gas phase was supplemented with single-point calculations using post-Hartree-Fock methods, e.g. coupled-cluster theory.[25]

fication has more recently been applied to some of the reactions here mentioned[49] using path-metadynamics with the global - and more accurate - collective variables introduced in Ref. 50. Umbrella sampling[51] was also employed for additional simulations in the neighborhood of transition states, aimed at a more accurate evaluation of the FEBs. DFT energies of the sampled configurations in the reactant and transition-state domains, lead to an estimate of the enthalpy barriers (ΔE^*), and, by subtracting the free-energy difference, also of the entropy contribution to the FEBs. It is not obvious, in principle, whether entropy changes along the process act so as to facilitate (accelerate) or to impede it (slow it down).

The models for the solution were set up so as to include a few solvation shells and also a number of CO_2 and amine molecules, depending on the concentration we wanted to investigate. Most calculations of diluted amines and their derivative were performed with periodically-repeated cubic cells containing about 125 water molecules. In the case of MEA at 30 % wt., samples of different sizes were used to ensure minimum effects of the boundary conditions, within the statistical error intrinsic to the free-energy calculations. Most simulations referred to models consisting of 30 amines, 15 CO_2 and 237 water molecules. Regarding the specific approximation for the exchange-correlation functional, the BLYP-D2[52,53] was selected, including Grimme's semi-empirical corrections for long-range dispersion, after a series of tests on the structural properties and the relative stability of conformers of amines, carbamates, and di-amines in the gas phase, both isolated and in water complexes. Variations of the complete MTD results on passing from BLYP-D2 to the PBE-D2 [53,54] were examined in the case of the diluted MEA sample[28] and found to be not significant within the accuracy of the calculations.

Table 1: Some characteristics of quantum-chemical calculations of the CO_2-MEA(aq) system. All models contain one CO_2. SBC stands for spherical boundary conditions (radius in parenthesis (Å)). PBC stands for periodic boundary conditions with cubic cell of edge given in parenthesis (Å). *OPT*=geometry-optimization. *DYN*=dynamics. Z=zwitterion. For DFT calculations, the xc functional is specified. TIP3P is the force field of the QM/MM approach.

	MODEL		METHOD		Reference
	$\#MEA$	$\#H_2O$	*OPT*	*DYN*	
Solvent					
Implicit					
PCM^a	2	1	B3LYP^b		[23]
PCM^a	0 or 1	1 or 0	B3LYP^b		[24]
PCM^a	1	2	B3LYP^b		[34]
CPCM^c	1 or 2	-	B3LYP^b,		[25]
COSMO^d	1	0 or 2	PW91^e		[27]
SMD^f	1	-	B3LYP^b & MP2	-	[30,36]
Explicit					
SBC(20)	1			B3LYP^b/TIP3P^g	[25]
PBC(8.639)	1+1Z	16	-	PW91^e	[27]
PBC(12.45)	1Z	59	-	PW91^e	[31]
PBC(9.278)	2	20	-	PBE^h	[34]

^{a} Ref. [55], ^{b} Ref. [56], ^{c} Ref. [57], ^{d} Ref. [58], ^{e} Ref. [59], ^{f} Ref. [60], ^{g} Ref. [61], ^{h} Ref. [54]

Table 2: DFT-MD plus MTD: Lowest values estimated for the free-energy barriers ΔF^* of the simulated reactions in MEA and AMPD solutions at room temperature, and corresponding enthalpy barriers ΔE^* (kcal/mol). The values refer to models of similar size and of the same (30 % wt.) concentration. From Ref. 38. In all cases the BLYP-D2 functionals. For the dependence on the conformer of the reactant, on temperature and model-size, we refer to the original articles. In the case of MEA, values in parenthesis refer to the dilute solution as in Ref. 28. Errors are estimated as ± 2-3kcal/mol.

Amine	ΔF^*	ΔE^*
Zwitterion formation		
MEA	14 [15]	12 [12]
AMPD	15	13
Zwitterion deprotonation		
MEA	8 [8]	12
AMPD	11	18
Carbamic acid deprotonation		
MEA	8	18
AMPD	10	20
CO_2 release from carbamate		
MEA	46	60
AMPD	36	52
CO_2 release from zwitterion		
MEA	7 [8]	25
AMPD	7	23
Deprotonation of protonated amine (AH^+)		
MEA	16	17
AMPD	13	15

2 Overview of the Results

2.1 Zwitterion and Carbamic Acid: Formation and Deprotonation

In the earliest work,[21] the authors propose that the progressive approach of CO_2 to MEA simultaneously drives a "gradual proton transfer" to a water molecule acting as the base. In this way, the formation of a zwitterion or any other intermediate is excluded. On the other hand, the formation of the carbamate is argued to require an activation barrier, which is however not intrinsic to the molecules but should be associated with either the displacement of water molecules in the solvation shell of the amine group or the approach of a base molecule (water or another MEA) to the amine.

Subsequent studies, using molecular structures and implicit solvent models, resulted in different predictions for the formation of the zwitterion , depending on their specific characteristics (see Table 1). It is found either to happen via barrierless routes[27] or to imply activation barriers of values up to ∼13kcal/mol.[25,36] In Ref. 25, a non-negligible dependence is emphasized on the choice of the cavity radius in the PCM, namely ranging from 5 to 12 kcal/mol. The higher values are in agreement with the estimates from experiment, as mentioned above.[47]

Deprotonation of the zwitterion ((2b)-forward) in favor of another MEA acting as proton acceptor is the process most frequently investigated. In most cases, this reaction was predicted to be barrierless[2], both in the absence of water[24,25] and in the presence of one near-by explicit water that behaved either as passive spectator[23,24,27] or as mediator of the reaction.[34] Also in a DFT-MD simulation of a zwitterion immersed in water[31] (see Table 1 for details) - namely in the absence of other MEAs - deprotonation of the zwitterion was observed to take place "instantly" via a Zundel-ion transient. However, the authors remarked that this especially rapid event was probably due to the "beneficial local water structure".

The route sketched in Eqs. (3a) and (3b) to carbamate from carbamic acid has been

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[2] We consider immaterial any claim of energy barriers of about or less than 1 kcal/mol because inferior to the accuracy of any calculation.

studied more rarely. Molecular calculations with hybrid solvent models (Table 1) predicted sizable energy barriers for the formation of carbamic acid, but through different pathways. In Ref. 25, the reaction in (3a)-forward is seen to involve the zwitterion as intermediate:

$$CO_2 + RNH_2 \rightarrow RNH_2^+COO^- \rightarrow RNHCOOH \text{ (3a')}$$

and to require the "catalyzing" action (not direct participation) of two (explicit) water molecules to decrease the energy barrier from 37.4 kcal/mol to 13.6 kcal/mol. We notice that in the same study, proton transfer from the zwitterion to another MEA was instead found to happen spontaneously and through "direct abstraction". Other DFT calculations[27] (Table 1) showed that the mediating action of a water molecule was necessary to transfer the proton from the zwitterion and an energy barrier of 11.8 kcal/mol had to be surmounted. Subsequent carbamic acid deprotonation and proton transfer to another MEA - according to (3b) - were both found to be barrierless and not needing the action of water. Spontaneous deprotonation of the carbamic acid and no direct intervention of water molecules is also the result of the cluster model of Ref. 34.

Our *ab initio* MD plus MTD simulations disagree with many of the above results.

I. The only consensus is about the zwitterion formation, which does not involve the intervention of water molecules as mediating agents and corresponds to an enthalpy barrier of 12 ± 3kcal/mol (Table 2), in agreement with the interpretation of empirical data.[47] In line with the analysis of forward and backward kinetic measurements,[62] our results also indicate that entropic effects tend to contrast CO_2 uptake. The quantitative understanding of the energy barrier is however challenging. As shown in Figure 2, the solvated hydrophobic CO_2 transforms into the hydrophilic carboxylate group of the zwitterion. Therefore, there is certainly an intrinsic contribution of the donor-acceptor binding complex, as shown for example in the CO_2 bending (Fig. 2 (b)), but also one associated with the solvent. The solvation shell of the amine group, invoked in Ref. 21, consists indeed of only one hydrogen bond (HB). On the other hand, the approaching CO_2 is accompanied by the breaking of the

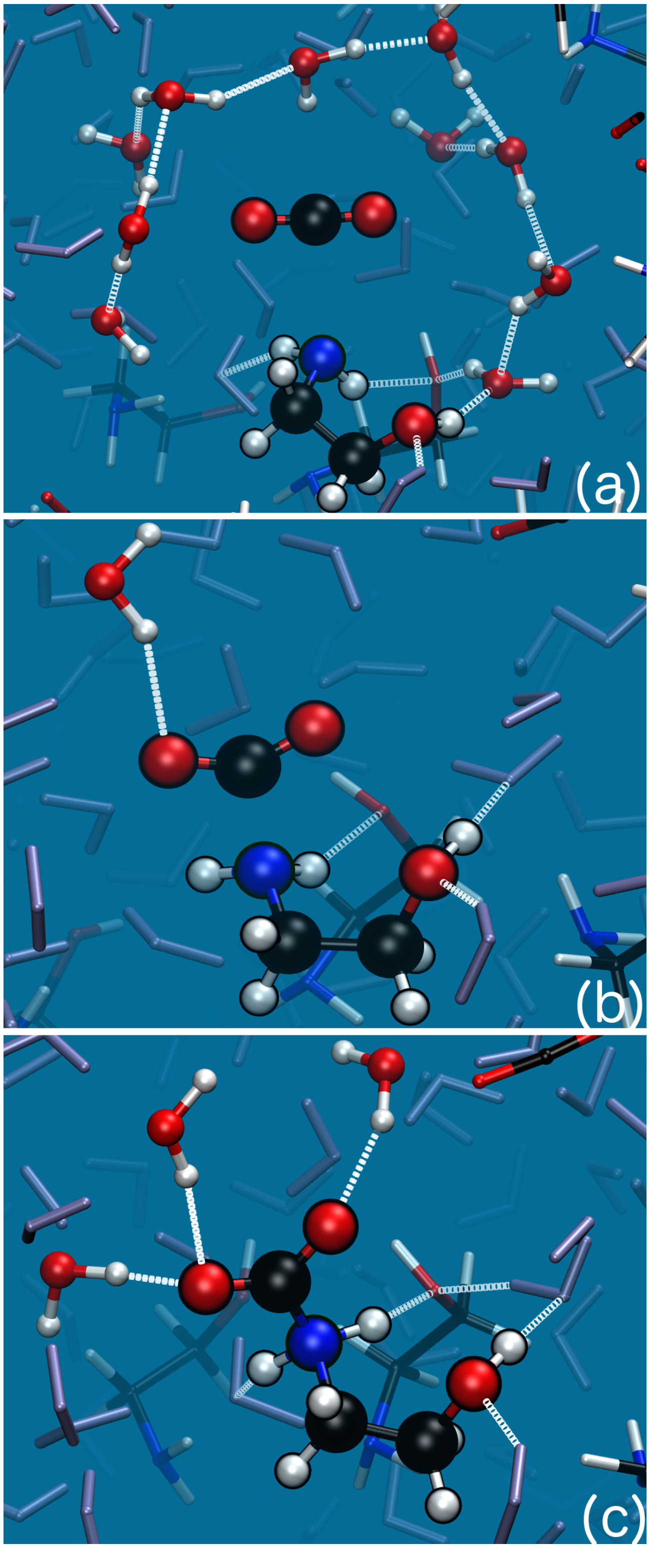

Figure 2: MEA solution: Snapshot of the formation of the zwitterion. From Ref. 33

HBs of the water cage around the solvated molecule (Fig. 2 (a)). Figure 3 illustrates the deformation of an electronic state on the amine, involved in the process.

II. Both in highly diluted solutions (3% wt.) and in those of practical interest (30% wt.), none of the unbiased MD, at 300K and at 400K, revealed sign of instability of the zwitterion for at least 15 ps after equilibration; when coupled with MTD, deprotonation ((2b)-forward) was indeed found to occur with a relatively high FEB, namely of ~ 10 kcal/mol. More precise values are reported in the original articles and recalled in Table 2. Also at 30% wt. concentration, the proton is transferred to a water molecule, thus generating a hydronium. Shorter or longer proton wires then form, depending on the specific simulations, and eventually lead to the formation of a protonated amine, as shown in Figure 4. The steps following deprotonation are all barrierless. This same scenario was found in all our simulations, namely for different conformers of MEA[33] - and different size models - and also for AMPD conformers[38] and for NH_3.[49]

III. As mentioned above, our simulations were not biased by pre-selected products. Indeed, once freed from the amine - thus transformed into a carbamate anion - via water the proton can also bind to one of the oxygens of the carboxylate group and generate a carbamic acid. This observation has lead us to propose the zwitterion as intermediate/transient species also for the formation of carbamic acid.[38] Moreover, our estimate for the deprotonation barrier of both MEA and AMPD carbamic acid is very close to that of the corresponding zwitterion (see Table 2). Proton migration towards another amine is observed to happen spontaneously through the water network and can be slowed down, in particular, by the other oxygen of the same carboxylate ion. Again, in contrast with Ref. 25, the direct participation of water molecules is then needed, both as proton acceptors and donors.

On the basis of the FEB calculations, the formation of carbamic acid from the zwitterion would have the same probability as that of carbamate, and can indeed be considered a process that slows down the formation of carbamates. We have observed it only in few of the equivalent trajectories, namely in AMPD and also in diluted NH_3.[49] However, from our

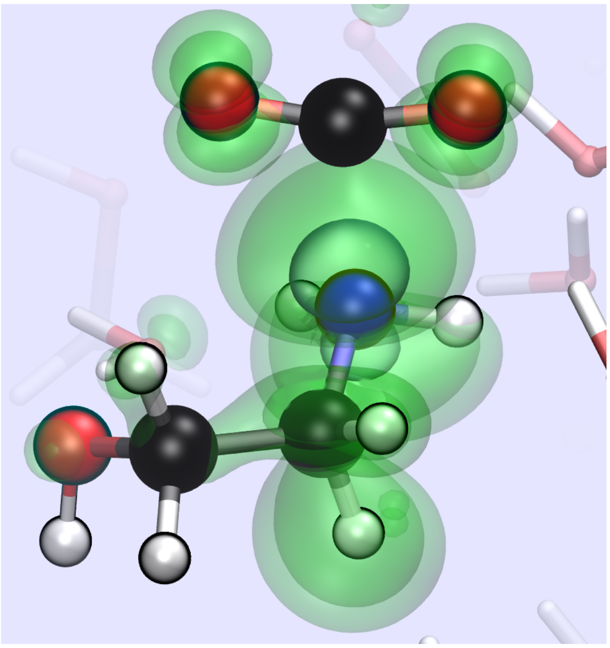

Figure 3: MEA solution: probability density corresponding to the one-electron state mainly involved in the formation of the zwitterion, in a configuration of the TS domain. Isosurfaces: 0.002, 0.005, 0.05 e/(a.u.)^3.

observations, we deduced that the water environment is responsible for the happening of one or the other pathway and that carbamic acid might be more probable - as first landing site for the proton - in the case of sterically-hindered amines, in which additional hydrophobic groups reduce the availability of near-by water molecules and the number of accessible paths for the proton towards other amines.

In summary, from our simulations of the reactions in MEA and AMPD, and contrary to most previous predictions: the zwitterion formation ((2a) forward) is an activated process in which water does not participate directly; zwitterion deprotonation - leading to carbamate - is an activated process, and is followed by barrierless diffusion of the proton through the HB network of water (Grotthuss mechanism) leading to the formation either of a protonated amine (((2b) forward) or of carbamic acid ((3a) forward); proton transfer from the latter also requires overcoming a FEB close to that of the zwitterion. We also emphasize that at 30% wt. concentration, MEA units tend to be separated by water molecules that act as proton acceptors. Therefore direct abstraction of the proton by another MEA is an improbable event. Moreover, from Table 2, one can infer that the likely rate limiting step for the generation of the carbamate (anion) plus protonated amine is the zwitterion formation. This conclusion agrees with those of previous studies, but in the latter it was motivated from the (incorrect) prediction of a barrierless deprotonation of the zwitterion.

We try to understand the reasons for the mentioned discrepancies between the results of our and previous calculations. The absence of any crucial information on the protocol of previous MD simulations - cited above - and in particular on equilibration times does not allow for any careful evaluation of their validity. The small size of the periodically repeated cells is only one of the parameters that has certainly influenced the results. Indeed, by creating identical replicas, PBC introduce an artificial order in the system; therefore, special care must be taken in deciding their size. This issue is especially critical in our case, namely of a liquid solution, characterized by structural and dynamical disorder and changes of the charge state of amines/amine derivatives and water molecules during the reactions.

On the other hand, quantum-chemical calculations of simple molecular clusters intrinsically tend to average-out the effect of water and underestimate its role. The use of a continuum model for the solvent - which is fundamental to ”stabilize” ionic configurations - is appropriate for cases of highly diluted solutions but only captures the average electrostatic aspects of the interaction with water. Solvation of the amines and their derivatives is indeed helped by the formation of HBs at the hydrophilic functional groups (-NH, -NH_2, -COH, -COO). Given that, as demonstrated by our simulations, water molecules well beyond the first solvation shell participate in each reaction, adding only one or two near-by water molecules is not sufficient to represent the solute-solvent interaction.

Moreover, the reorganization of the water HB network that accompanies the development of any of the reactions in (2) and (3) cannot be ignored. With the exception of the CO_2 uptake in the zwitterion, the entropic contribution is shown to be essential and strongly reduce the FEBs at room temperature. Therefore, also the effect of temperature cannot be neglected and cannot be trivially predicted via extrapolation from static calculations.

We also notice that the barriers reported in previous work are enthalpy barriers. The contribution of the vibrational entropy of the amines was apparently included in one case[25] although its value was not documented. Our simulations have found that the entropy changes due to the molecular components, other than water, are negligible.[33]

2.2 CO_2 release and amine regeneration

Regarding the regeneration of the amine, it is generally considered as taking place directly via CO_2 release from the carbamate and on this basis trends on the relative stability are discussed. Our simulations for MEA and AMPD show that the N-C bond breaking in the carbamate requires overcoming a barrier of the order of tens of kcal/mol (see Table 2) and the loss of CO_2 is accompanied by the recovery - from water - of the proton at the amino group.

On passing from MEA to AMPD, the carbamate is known to be less stable: NMR measurements, taken at 20 wt. % and 313K, detected it only at early stages of CO_2 loading[63] whereas it was not observed in others taken at 0.04 wt. % and about room temperature.[64] As shown in Table 2 the FEB for the loss of CO_2 decreases significantly from MEA to AMPD solutions, i.e. by ~10 kcal/mol, and this difference is of enthalpic nature, which is a sign of a weaker amine-COO bond, as expected on the basis of steric hindrance.[64] However, in spite of the important entropy contribution associated with the reorganization of the water molecules so as to host the hydrophobic molecule, the FEB remains **irrealistic** for both amines.

On the other hand, not surprisingly, CO_2 dissociation from the zwitterion involves a much lower FEB. Therefore, it is natural to propose that the most probable release event originates from the zwitterion[33,38] via the reverse reaction in (2a):

$$\mathrm{RNH_2^+COO^-} \rightarrow \mathrm{CO_2} + \mathrm{RNH_2}$$

as ultimate of a three-step mechanism, namely following the deprotonation of RNH_3^+ and the protonation of the carbamate at the N-site (see Figure 5). In this sequence, the

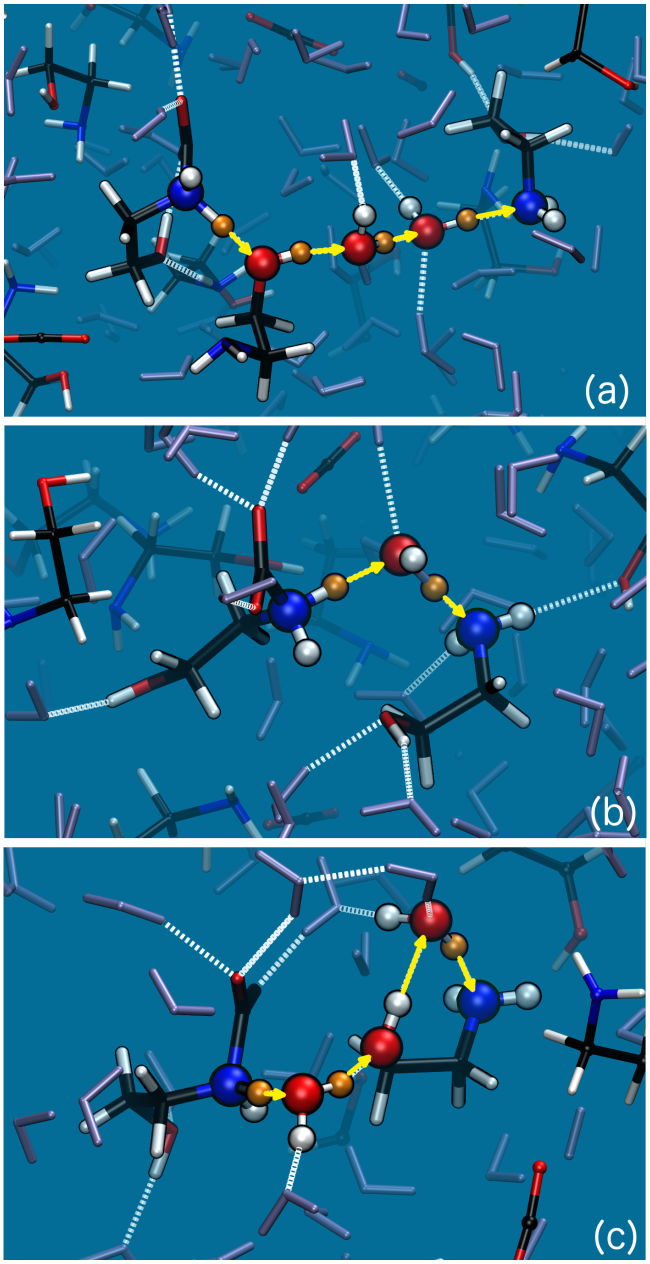

Figure 4: MEA solution - Snapshot of the deprotonation of the zwitterion - generating a carbamate - and different pathways leading to a protonated amine. The mediating action of water is emphasized (the golden sphere illustrates the migrating proton). From Ref. 33

deprotonation of RNH_3^+ would be the rate-limiting step, as can be deduced from comparison of the FEBs in Table 2. Naturally, whatever mechanism leading to an increase of the acidity of the solution after uptake, is likely to recover the zwitterion and thus help to liberate CO_2.

Indeed, this is the - not unexpected - result of Ref. 34 where 1000K-MD applied to a small and highly acidic model, with three free protons added to a cluster of two MEA-carbamates and twenty water molecules. Still a rather complicated series of events was described. A protonated carbamic acid (RH_3NCOOH) formed with a three-fold-hydrogenated nitrogen, which spontaneously lost the extra-proton and also the one bound to the carboxylate group. The simultaneous configurational change, including formation of an internal "HB" between one of the hydrogens of the amino group and the alcoholic termination, lead to the COO release.[3] Based on this observation, CO_2 release from the zwitterion was suggested as a relevant mechanism for the amine regeneration. In spite of this similar final suggestion, clearly the motivation is very different from that emerging from our simulations.

We notice that the FEB of the release from the zwitterion (Table 2) does not change from MEA to AMPD, within the accuracy of the calculations. Indeed, understanding the behavior of AMPD is especially challenging. As already discussed in the pioneering work of daSilva et al.,[22] several characteristics may determine the relative stability of carbamates, including not only steric factors - as often argued and that alone could not explain the difference of AMPD and AMP - but also solvation energies. In particular, in Ref. 30, a correlation is searched with electronic and/or structural parameters of the parent amine molecules - like the charge on nitrogen or the "intramolecular HB distance". In the case of AMPD, however, this search was not successful. As mentioned above, we have suggested another effect of the substitutions leading from MEA to AMPD, namely that, by changing the water environment, they may favor the formation of carbamic acid, and thus slow down the rate of formation of carbamates. More conclusive results will have to wait for an analogous study of AMP

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[3] These so-called ring conformations of the amines are stable or metastable in gas phase but unstable in water. Moreover although the H–O distance is compatible with a typical HB, the angle is not. Therefore the definition of HB does not seem appropriate.

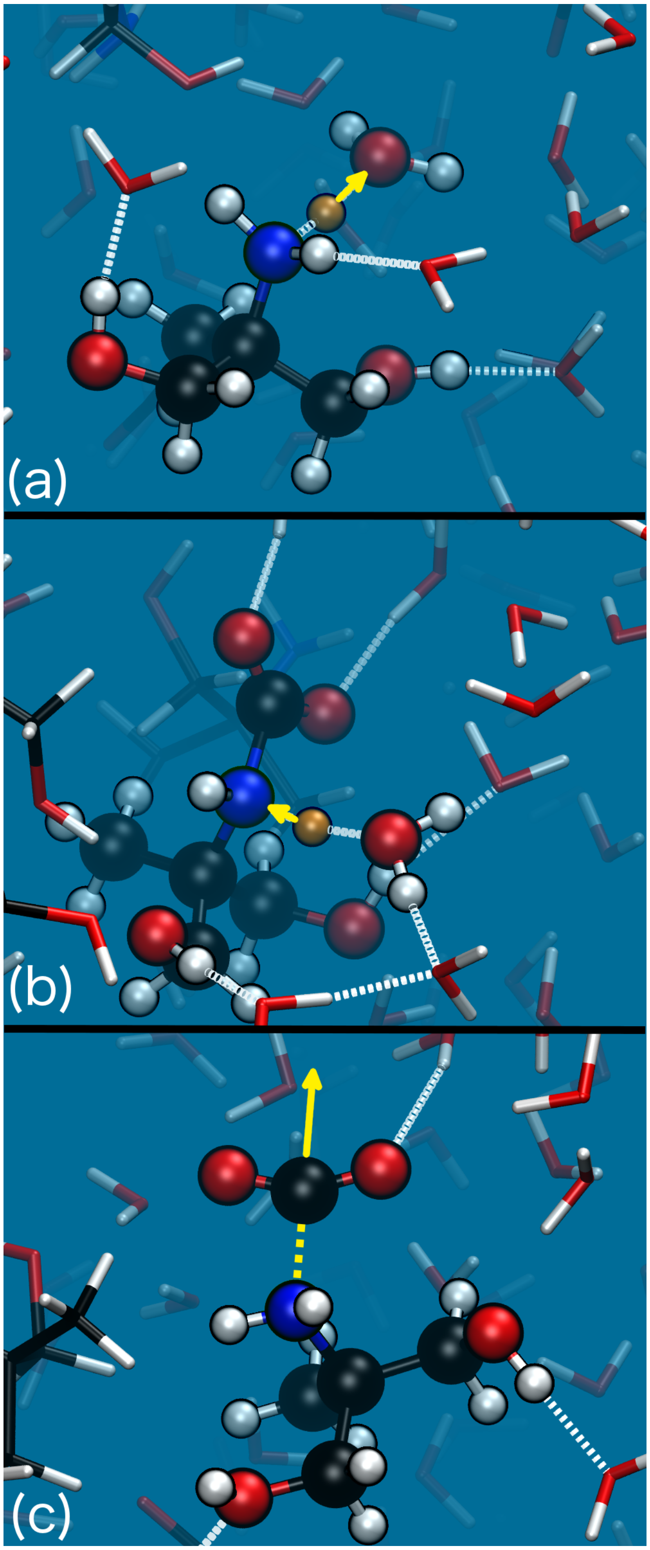

Figure 5: AMPD solution - Snapshots of the three main reaction steps leading to the release of CO_2 in solution. From Ref. 38

solutions.

2.3 Further results and remarks

There are other ways in which one can exploit the results of *ab initio* MD simulations, and especially the information contained in the trajectories of the solutions at equilibrium. By comparing structural and vibrational properties of our model solutions for the reactant (solvated amines + CO_2 molecules) and for the product (i.e., after carbamate formation), we could interpret experimental data from X-ray diffraction and infrared spectroscopy, both aimed at monitoring the presence of carbamates with increasing CO_2 loading.[32] Our results also demonstrated that previous attempts to interpret the vibrational spectra with calculations of gas-phase molecules were inadequate. This type of application could indeed become an interesting tool for the diagnostics of the products of the reactions discussed above.

Comparing the relative stability of reactants and products in the gas-phase, also modified by the continuum model for water, is easy but the validity of the results remains dubious. For example, the zwitterion can also turn out to be more "stable" than the reactant.[24] Indeed, one should be able to represent the systems in the liquid solution at equilibrium and calculate the difference in Gibbs free-energy. The duration of our simulations (each of the order of 10 ps) does not allow for a quantitative assessment. However, using the FEBs of both forward and inverse reactions, an estimate could still be obtained, and proved the consistency of our computations. For example, in the case of MEA we obtained an overall negligible free-energy difference between the reactant (CO_2+MEA) and the product (carbamate+$MEAH^+$) solvated. Within the precision of our calculations, this result is in agreement with experiment.[62] Moreover, the zwitterion intermediate was indeed less "stable" than reactant and product and its population smaller by a factor 10^{-5}-10^{-6}. The latter is consistent with the failure of any experiment to detect its presence. Also, the population of carbamic acid turned out to be similar to that of the zwitterion.

3 Conclusions

The scope of the critical review presented above was mainly that of creating awareness of the limited understanding of the fundamental chemistry of CO_2 capture in industrially relevant systems like amine aqueous solutions. This situation may ultimately hamper the possibility of improving this technology, which is crucial for utilization on the large-scale. Therefore, extensive and high-quality computational work in this field should be encouraged.

The dependence on the method was emphasized. Indeed, as long as the structural models for the system in solution are not realistic, also the use of sophisticated quantum-chemical approaches is not useful.

DFT-based MD aided by efficient sampling methods is a convenient way to study chemical reactions in solution, provided however that the underlying structural model and the protocol of the simulations are under control. As clarified above, this type of approach has already unveiled completely new scenarios, in which the role of water - previously strongly underestimated - was established as essential not only in stabilizing charged species but in facilitating the development of all reactions, and proton loss from any of the amine-derivatives (zwitterion, carbamic acid, protonated amine) was found to be an activated process with FEBs of $\sim$10 kcal/mol. Conclusions were based neither on the use of pre-arranged configurations for the reactants and products nor on single simulations. Series of calculations were performed in different conditions, which have confirmed not only reaction pathways but, within the accuracy of the calculations, also the values estimated for the FEBs.

However, we believe that several methodological problems must be resolved before reliable quantitative predictions can be made and computational results can be of help to experimental efforts towards technological improvement. Above all, the so-called sampling problem. Quantitative assessment of the relative thermodynamic stability of reactants, intermediates and products in solution, and comparison of relative probability of different possible reaction channels, especially when contrasting different amine-based solvents, requires longer times and more extensive exploration of the configurational space.

Also, the use of hybrid DFT functionals and non-empirical van-der-Waals DFT functionals should be encouraged, especially for a more accurate description of the dynamics of water.

In conclusion, we believe that computer simulations can become an essential tool for materials and process design, not only by elucidating the reaction mechanisms and the specific role of solvent,[65,66] but also in providing quantitative information. Especially, the next "grand challenge" is the evaluation of the kinetic rates directly from the simulated trajectories.

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