Physical Absorption of Green House Gases in Amines: The Influence of Functionality, Structure and Cross Interactions

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Monte-Carlo simulations were performed in the isothermal-isobaric ensemble (NPT) to calculate the Henry constant of methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2) in pure H_2O, amines and alkanolamines using the classical Lorentz-Berthelot (L-B) combinig rules. The Henry constants of N_2O and CO_2 in water are highly overestimated and motivated us to propose a new set of unlike interactions. Contrarily, the Henry constant of N_2O in MEA is underestimated by around 40%. Again, a new re-optimized cross unlike parameter is proposed to reproduce the constant to within 10%. An analysis is given of the relationship between the physical absorption of these gases and the chemical structure or functionality of 12 molecules including amines and alkanolamines using the anisotropic united atom intermolecular potential (AUA4).

Finally, the solubility of N_2O in an aqueous solution of monoethanolamine (MEA) at 30% (wt) was also studied. Using the re-optimized parameters along with the L-B mixing rules to account for the MEA+H_2O unlike interactions estimate a Henry constant within 7% of accuracy with respect to the experimental value. The very good agreement without additional refittings for the MEA+H_2O system may be attributed to the good excess properties predictions found in previous works for the binary mixture (MEA+H_2O). However, further work including more alkanolamines in aqueous solutions at several concentrations is required to verify this particular point.

Keywords: CO_2 capture processes, N_2O analogy, Green house gases, Molecular simulation, Amines absorption, Combining rules.

1 Introduction

Due to increasing environmental concerns, gas emissions are considered to be one of the most important problems that needs to be overcome during the coming decades. Besides greenhouse gases (GHG), sulfur containing compounds present in natural gas also require special attention since they can be extremely harmful and even lethal for living organisms. In the case of natural gas sweetening technologies, there are several well known processes that have been proposed to help control these emissions including: adsorption, membrane permeation, chemical conversion and condensation. The selection process of the technology to be used depends on many factors, such as the level of impurities

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in the feed-stream and the physical-chemical features of the gas[1]. In particular, the absorption process based on alkanolamines as a chemical solvent is one of the most widely extended processes around the world which is shown by the large number of installed plants and the variety of processes offered in the market from different companies.

In the case of GHG, a strong effort is currently being dedicated either to improve the current methods or to develop alternative processes in order to reduce the emissions. This is particularly true for carbon dioxide (CO_2), which is considered as one of the major contributors to global warming. Different alternatives have been proposed including physical absorption by means of ionic liquids or chemical absorption using alkanolamines. Zeolites and metal organic frameworks have been also considered as possible candidates. A detailed description of all these alternatives including some advantages, disadvantages and their maturity can be found in a review by MacDowell *et al.*[2]. D'Alessandro *et al.*[3] have also presented a review on this area but focused on microporous materials.

Up to now, there is no definitive answer about which is the best technology and it appears that there is no unique solution to solve the problem. However, and despite the high energy requirements for solvent regeneration, alkanolamine absorption processes are considered to be an attractive choice. Recent experimental studies[4–6] have shown that other amines, not necessarily alkanolamines, such as linear aliphatic amines, multifunctional amines or cyclic amines also present good absorption rates of CO_2. Unfortunately there are currently no criteria that clearly specify how to decide the best solvent choice among a large number of possible good candidates. It is thus clear that a lot of questions still need to be answered. Here molecular simulation is able to provide both fundamental information about the physical-chemical processes in these systems as well as quantitative predictions of the thermodynamic and transport properties and, along with the necessary experimental information, can clarify many of these aspects.

One of the advantages of studying the absorption process using amines as solvents is that, being the most mature technology available, experimental information can be found in the literature for many properties over a large range of temperatures and pressures and at different aqueous molar fractions. Nevertheless, only a few molecules have been studied, the most important ones being the alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and more recently some hindered alkanolamines such as AMP (2-methyl-2-amino propanol).

The aim of this work is to study the physical absorption of several GHG such as methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2) in different solvents including: pure H_2O, pure amines, pure alkanolamines and one aqueous solution of MEA at 30 % (wt). The physical solubilities of these gases are evaluated through the Henry constant which is mainly calculated using the so-called Widom insertion technique. Furthermore, the effect of the chemical structure on the physical solubility will be also evaluated. In the case of CO_2 in the presence of amines a reaction occurs, however, in the present study this reaction is ignored and the Henry constant refers only to the physical part of the absorption. To the best of our knowledge, no prior molecular simulation studies have focused on this type of calculation.

The accurate estimation from molecular simulation of physical-chemical properties lies critically on the ability of the force field to correctly represent the molecules of interest. Consequently, for this work, we use our recently proposed force fields based on the anisotropic united atom approach. These force fields include primary[7], secondary and tertiary amines[8], multifunctional amines such as diamines and triamines, and also primary, secondary and tertiary alkanolamines[9]. So far we have checked the transferability for more than 30 molecules obtaining in general a good agreement with experimental results. The force fields are able to correctly reproduce different thermodynamic properties such as densities, vaporization enthalpies, normal boiling points, critical coordinates and surface tensions.

This paper has been divided as follows: in the second section, the features of our AUA4 force fields as well as the computational details of the simulations are given. In the third section, we present the results obtained for the Henry constants. Firstly, we present the simplest systems consisting of binary mixtures of H_2O-N_2O and H_2O-CO_2, secondly, several amine-N_2O systems are evaluated, and finally, a ternary mixture of MEA-H_2O-N_2O is also studied. For all these cases polarization will be accounted for by a re-optimization of the cross interaction between unlike molecules. In the fourth and last section a discussion about the results is presented as well as conclusions and prospects.

2 Force field features and computational details

Several well known force fields for CO_2, CH_4, N_2O, H_2O were evaluated using the different possible combinations. Namely, SPC/E[10] and TIP4P/2005[11] for H_2O, EPM2[12] and TraPPE[13] for CO_2, the Moller *et al.* model for CH_4[14], and the Lachet *et al.* model for N_2O[15]. It is worth pointing out that in the N_2O Lachet *et. al* model each nitrogen has associated different ϵ and σ parameters. As mentioned in the previous section, the AUA4 force field was used to account for all the amine molecules. All the parameters and details concerning the force fields are given in the supporting information section.

Briefly, the main features of the AUA4 force field are: i) all bonds are considered to be rigid, ii) groups of three connected atoms interact by means of a harmonic bending potential, iii) groups of four connected atoms interact by way of a torsional potential which is a function of the corresponding dihedral angle iv) interactions between force centers separated by more than three bonds are taken into account via the same L-J potential as for intermolecular interactions v) in case of multifunctional amines (such as diamines or alkanolamines), intramolecular electrostatic interactions, have been modeled through the local dipole approach proposed by Ferrando *et al.*[16]. Such an approach has been already used in previous works for multifunctional amines. The advantages when using the local dipole approach are basically that neither additional interaction terms nor scaling factors need to be considered. In this work we have studied in total 12 amines including linear amines ethylamine (EA), propylamine (PA), *n*-butylamine (BA) and *n*-hexylamine (HA). Branched and hindered amines *iso*-butylamine (i-BA) and *tert*-butylamine (t-BA), respectively. Secondary and tertiary mono-functional amines Diethylamine (DA) and triethylamine (TA). The bi-functional amine ethylenediamine (EDA) and finally the primary, secondary and tertiary alkanolamines monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), respectively.

For short molecules like ethylamine or propylamine, nearly all simulations were performed using 50 million Monte Carlo Steps (MCS) for the equilibration period while for the production part a total of 700 million MCS was employed for nearly all the molecules. Every MCS corresponds to a simple MC move. For longer molecules such as diethanolamine (DEA) and methyldiethanolamine (MDEA) longer simulations were required, ranging between 700 and 950 million MCS. For pure amine systems a total of 300 molecules were used in the simulation box. For the MEA aqueous solutions, the number of H_2O

molecules was calculated in order to obtain 30% (wt) of amine which is a typical value of the CO_2 capture processes. Finite size effects were tested by increasing the system size up to 600 molecules for EA and MEA, but no significant differences were found in the radial distribution functions, liquid densities or Henry constants. Simulations were performed in the isobaric-isothermal ensemble (NPT) at atmospheric pressure and temperatures from 300K to 360K, which corresponds to typical conditions of conventional absorption processes.

The simulations were performed using the GIBBS Monte Carlo (MC) code developed by IFPEN and Orsay University[17]. Periodic boundary conditions and the minimum image convention were used. To calculate the Lennard-Jones (L-J) interactions between force centers, a spherical cutoff equal to half of the simulation box was applied, while for long-range electrostatic interactions the Ewald procedure was chosen[18] with a maximum of 7 vectors in each direction of reciprocal space and with the scaling parameter $\alpha = 2$ in reduced units. In order to sample the configurational phase space, different MC moves were used, including: translations (20%), rigid rotations (20%), configurational bias regrowths (20%), insertion moves with positions and orientation bias (39.5%), volume changes (0.5%). For long amines such as MDEA, DEA, HA, EA, EDA, TA, internal rotations moves (i.e., the rotation of a force center around its nearest neighbors) were also used in order to improve the sampling for the intramolecular degrees of freedom of the molecules. The amplitudes of translations, rotations and volume changes were adjusted during the simulation to achieve an acceptance ratio of 40% for these moves.

Different well known methods are available in the literature to calculate free energies, for instance: free energy perturbations, umbrella sampling, expanded ensembles, transition matrix, and thermodynamic integration[19]. For this particular study the physical solubility was estimated using the Widom insertion technique. This methodology has been extensively used and details can be found elsewhere[18,19]. Briefly, the Henry constant (K_H) is related to the excess chemical potential (μ^E) by means of eq-1

$$\frac{\mu^E}{k_B T} = ln \frac{K_{\mathrm{H}}}{\rho k_B T} \tag{1}$$

where k_B represents the Boltzmann constant, T the temperature of the system and ρ the density of the solvent.

Thus, if the chemical potential is calculated, then the Henry constant can be directly estimated. According to the Widom particle insertion formula[18], the chemical potential is calculated from an ensemble average eq-2

$$\mu^E = -k_B T \ln \left\langle \frac{PV}{k_B T(N+1)} \exp\left(-\frac{\Delta U}{k_B T}\right) \right\rangle_{NPT} \tag{2}$$

where ΔU is the potential energy difference due to the insertion of the test molecule, P, N and V correspond to the pressure, total number of particles and volume of the system.

3 Results

3.1 H_2O-CO_2 and H_2O-N_2O binary systems

The Henry constant is intimately related to the molecular interactions between the solvent and the solute. From a molecular simulation point of view, gases in polar systems are particularly complex since their accuracy depends on whether the interactions between the unlike molecules are well represented or not. For this study, we started with the "simplest" cases which correspond to binary mixtures of CO_2-H_2O as well as N_2O-H_2O. NPT simulations were performed at several temperatures and atmospheric pressure using 300 molecules and 1400 million Monte-Carlo Steps (MCS). Finite-size effects were tested at 313K and 353K increasing the system size to 500 molecules but no significant differences were observed obtaining the same results within the error bars. The classical Lorentz-Berthelot combining rules were applied to calculate all interactions and all Henry constants values were evaluated by the Widom test particle technique.

Figure 1 shows the Henry constant values in (MPa) at different temperatures for the H_2O-CO_2 system for the following force field combinations: SPC/E-TraPPE, SPC/E-EPM2, TIP4P/2005-EPM2 and TIP4P/2005-TraPPE. Experimental information is also included to compare with[20–23].

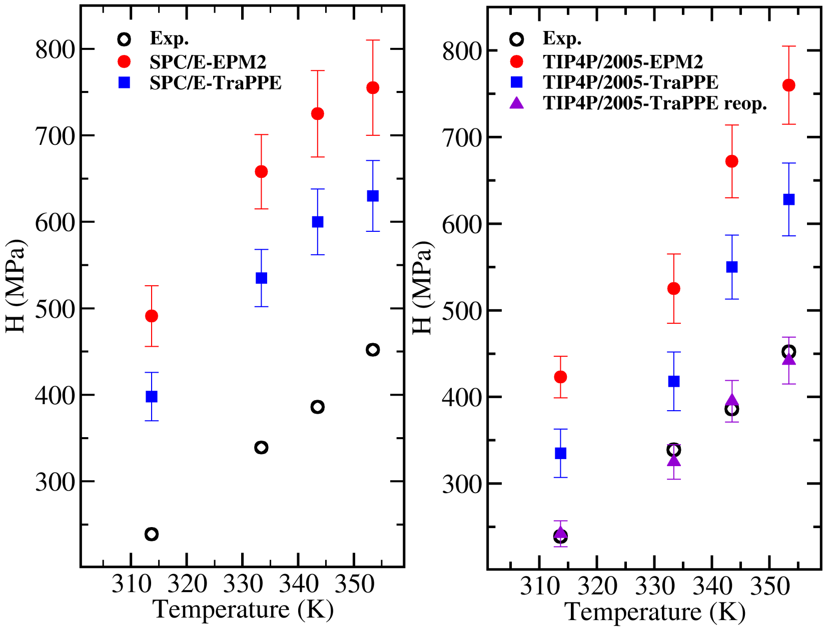

Figure 1: Henry constants at several temperatures for the H_2O-CO_2 binary system using the SPC/E (left) and the TIP4P/2005 (right) water models, TraPPE and EPM2 were used for the CO_2 molecule. Predictions using the reoptmized parameter $\epsilon_{C(CO2)-O(H2O)}$ are also shown (violet triangles). Experimental information was taken from the reported values of Hartono *et al.*, their experimental uncertainties are within 3%[22]

For the CO_2-H_2O system it is possible to observe that all the studied force field combinations highly overestimate the experimental value of the Henry constants. In general, the SPC/E water model gives the largest deviations of almost 100 % with respect to the experimental value. In the case of the TIP4P/2005 model, the Henry constant predictions show lower values but are also overestimated. For both cases it is possible to see that the TraPPE model gives a better estimate than the EPM2 model. Deviations can mostly be related to a poor representation of the unlike interactions between H_2O and CO_2. However, neglecting the chemical reaction that produces carbonic acid and its subsequent dissociation to bicarbonate and carbonate ionic species may also have contributed to the found discrepancies.

With regards to the N_2O-H_2O system two main features were found, see Figure 2. First of all, the Henry constant predictions are also overestimated, but this time the deviations are significantly lower than the ones obtained with the CO_2 models. In fact, the numerical values for the N_2O model are close to the CO_2 predictions but the agreement is better since the experimental Henry constant of N_2O in H_2O is higher than the one of CO_2 in H_2O. Second, the TIP4P/2005 water model gives a better agreement than the SPC/E model. Numerical results for both systems CO_2-H_2O and N_2O-H_2O are given in the supporting information section.

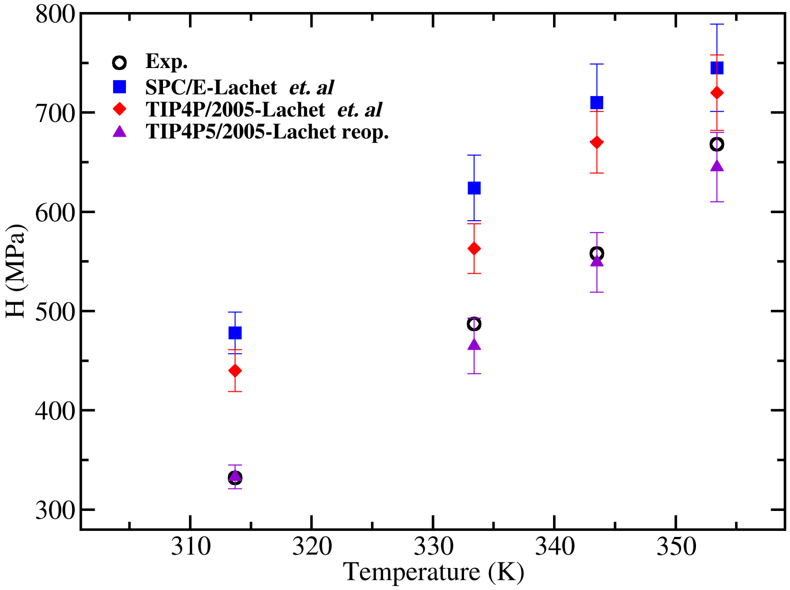

Figure 2: Henry constants at several temperatures for the H_2O-N_2O binary system using the SPC/E and the TIP4P/2005 water models. For N_2O the Lachet *et.al* model was used. Predictions using the re-optimized parameter $\epsilon_{N1(N2O)-O(H2O)}$ are also shown (violet triangles). Experimental information was taken from the reported values of Hartono *et al.*, their experimental uncertainties are within 3%[22].

Many articles in the literature have found that force fields which accurately reproduce the experimental properties of pure compounds can have important deviations when used for mixtures using combining rules such as Lorentz-Berthelot[24–29]. One of the main limitations of fixed-point charge force fields is the lack of polarization. In several cases it is believed that the cross interactions might be poorly represented using the standard Lorentz-Berthelot combining rules. However different alternatives can be considered in order to account for this deficiency. The most straightforward approach is based on modifying the mixing rules for the unlike interactions. In this work we require accurate predictions using the proposed models and, taking into account the inability of these models to predict values in agreement with the experimental information, we decided to re-optimize the unlike interactions for both binary systems using the TIP4P/2005 force field for water, the TraPPE force field for CO_2 and the Lachet *et. al* for N_2O. This force field choice is based on the better agreement with experimental data observed for these models. Another reason to choose TIP4P/2005 as a water model lies in the fact that previous works have shown that the excess enthalpies of the *n*-butylamine-H_2O and monoethanolamine-H_2O systems are in excellent quantitative agreement with the available experimental data[30,31].

In order to improve the model accuracy, a systematic procedure based on a sensitivity analysis was followed. Briefly, all the L-J cross interactions between unlike atoms (σ, ϵ) were changed so as to understand the most relevant effects of these changes on the Henry constant. At the studied conditions, it is found (results not given here) that the interactions with the highest sensitivity corresponds to the C(CO_2)-O(H_2O) for the CO_2-H_2O system and the N1(N_2O)-O(H_2O) for the N_2O-H_2O one. For the two studied binary systems it was found that the well-depth parameter (ϵ) had a higher sensitivity than the σ parameter. In some cases, such a result might be related to numerical differences between the L-J parameters. For instance, the σ and ϵ values for the carbon belonging to CO_2 are quite different from the oxygen belonging to the H_2O molecule.

Once the sensitivity analysis was performed, the C(CO_2)-O(H_2O) and N1(N_2O)-O(H_2O) parameters were re-optimized following a similar procedure to the one proposed by Orozco *et al.*[32] choosing the Henry constant as the target property. After an iterative procedure, a set of re-optimized parameters able to better reproduce the experimental Henry constant were found. Namely, $\epsilon_{N1(N2O)-O(H2O)}/k_B =$ 92.64K for the N_2O-H_2O system and $\epsilon_{C(CO2)-O(H2O)}/k_B = 60.82$K for the CO_2-H_2O. For the first case this corresponds to an increment of 8% in the ϵ value while for the second case the increment corresponds to 23% with respect to the L-B mixing rules. Table 1 summarizes the numerical Henry constant results using the re-optimized unlike parameters which can be also observed in Figure 1 and Figure 2 as violet triangles. The third column shows the ratio between the predicted Henry constants for CO_2 and N_2O, i.e., an evaluation of the use of N_2O as a non reactive analogous of CO_2. For the studied range of temperatures an average ratio of 0.71±0.04 was obtained which is in agreement with the average experimental ratio of 0.72 reported by Ma'mun *et al.* in the range of temperatures between 273K to 360K[33].

Force Field	H^{sim}(MPa)	H^{exp}(MPa)	$(H_{CO2}/H_{N2O})^{sim}$	T (K)
TIP4P/2005-N_2O	246±15	266-269	0.74±0.04	303.0
	333±18	325-332	0.72±0.04	313.7
	465±28	485-487	0.70±0.04	333.4
	554±30	558	0.72±0.04	343.5
	635±33	668	0.69±0.05	353.4
TIP4P/2005-CO_2	182 ±8	192		303.0
	240 ±10	239		313.7
	325 ±14	339		333.4
	399 ±18	386-392		343.5
	442 ±23	452		353.4

Table 1: Henry constants with re-optimized unlike interactions for Lachet N_2O and TraPPE CO_2 with TIP4P/2005 water models.

3.2 Pure amine-(N_2O, CH_4, CO_2) systems

Following a similar procedure to water, the Henry constants of CH_4, CO_2 and N_2O were calculated in several pure amine solvents using the NPT ensemble at atmospheric pressure and the Widom insertion technique. The corresponding chemical structures of the studied molecules are shown in Figure 3. The TraPPE force field was chosen to represent CO_2, Lachet *et al.* for N_2O and AUA4 for the amines and alkanolamines.

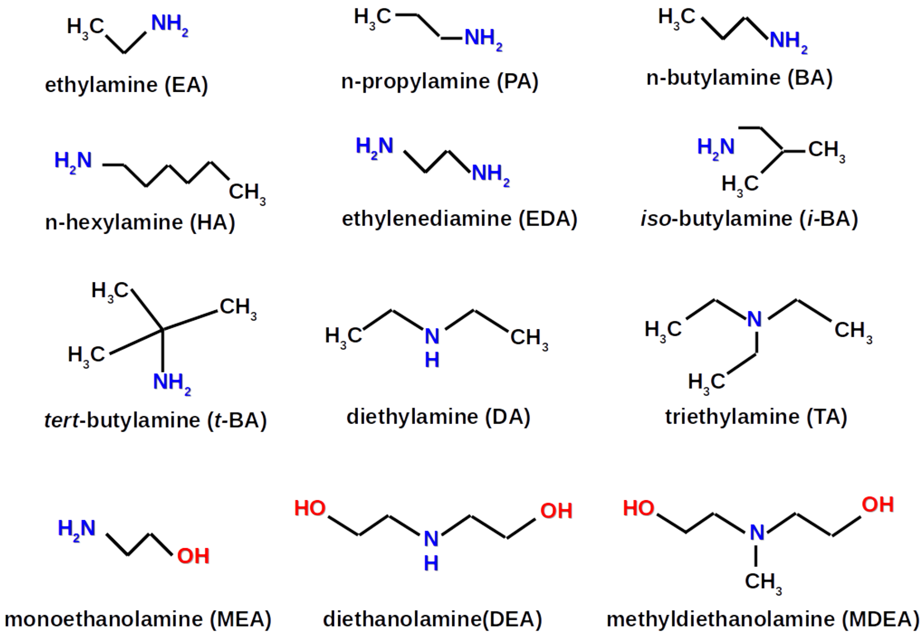

Figure 3: Amine molecules studied in this work. Abbreviations are given in parenthesis.

Figure 4 shows the Henry constant results in MPa for CH_4, CO_2 and N_2O for all the amine molecules shown in Figure 3. It is well known that CO_2 reacts in the presence of amines, however our simulations do not consider this effect. The results for CO_2 are presented principally to allow a comparison with N_2O and allow to distinguish between physical absorption and chemical absorption which may be required in process modeling. As shown, and unlike pure H_2O, the Henry constants of N_2O and CO_2 are quite similar in pure amines and significantly lower compared with the obtained ones in pure H_2O. To the best of our knowledge, there is only experimental information to compare with for the alkanolamines-N_2O systems[20]. Numerical values are given in the supporting information section.

From these results several features can be established. Firstly, at 300K, when increasing the number of carbons in the aliphatic chain of mono-functional primary linear amines the Henry constant for CO_2 and N_2O decreases. Nevertheless, since the numerical differences are very small it is not possible to establish a final conclusion taking into account the statistical uncertainty. Similarly, the Henry constants of CH_4 decrease as the aliphatic chain increases as well. In this case the numerical differences are more significant showing a direct relationship between the CH_4 solubility and the number of carbons in the aliphatic chain.

Secondly, when comparing the Henry constant for all the studied gases in linear amine *n*-butylamine

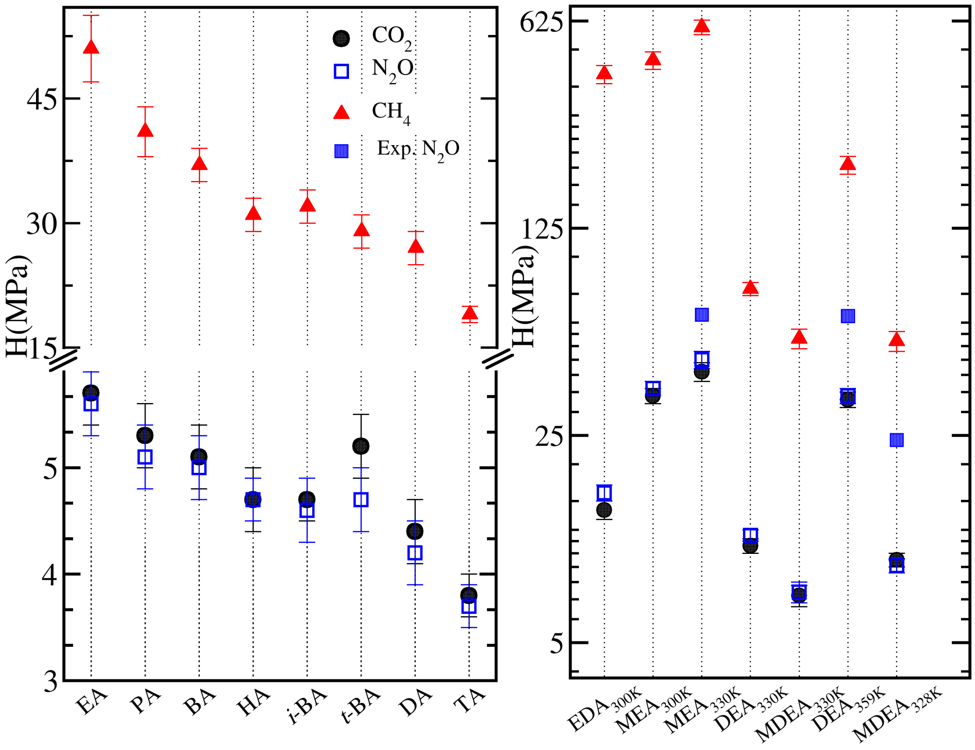

Figure 4: Comparison of the physical Henry constants in several pure amine solvents. Monofunctional amines at 300K (left), note there are two different scales. Multifunctional amines at several temperatures in logarithmic scale (right). Abbreviations corresponds to: EA ethylamine, PA *n*-propylamine, BA *n*-butylamine, HA *n*-hexylamine, *i*-BA *iso*-butylamine, *t*-BA *tert*-butylamine, DA diethylamine, TA triethylamine, EDA ethylenediamine, MEA monoethanolamine, DEA diethanolamine, MDEA methyldiethanolamine. Vertical dashed lines serves as a guide to the eye. Experimental values (blue filled squares) taken from Wang *et al.* the reported uncertainties of the experimental values are within 2% [20].

and isomers like *iso*-butylamine and the hindered *tert*-butylamine, no significant numerical differences can be appreciated. Therefore, at these conditions, it is possible to conclude that there is no relation between the chemical structure of isomers and their physical absorption. Comparing the first members of the homologous series for primary, secondary and tertiary amines, i.e., ethyl, diethyl and triethylamine, it is possible to see that for all the studied gases, the Henry constant decreases as the number of hydrogens of the amino-group are replaced by amine groups, giving the sequence TA<DA< EA. Interestingly, the Henry constant for CH_4 is numerically similar in diethylamine and *n*-butylamine which have the same number of carbons.

Thirdly, a comparison between mono-functional and bi-functional primary amines with a similar chain length (see Figure 3), e.g., *n*-butylamine (BA) and ethylenediamine (EDA) shows that the Henry constant of N_2O in EDA is ~ 3 times higher than the N_2O Henry constant in BA, and the henry constant of CH_4 in EDA is ~ 10 times higher than the CH_4 Henry constant in BA. This result implies that for the studied gases, the presence of more than one amino group significantly decreases the physical solubility. On the other hand, if instead of two amino groups (EDA) a hydroxyl and an amino groups are considered, as in the case of MEA, the Henry constants values are numerically higher for all the studied gases. This means that the effect of the hydroxyl group is stronger than that of the amino group giving the following sequence in terms of Henry constant BA < EDA < MEA. This result is in agreement with the experimental results recently reported by Ma'mun *et al.* in which pure multifunctional amines like di-amines and tri-amines showed higher N_2O solubilities than pure alkanolamines[33].

Considering only alkanolamines, at 330.8K where experimental information is available for MEA, important differences can be noted between MEA, DEA and MDEA. As can be seen, the highest Henry constant value corresponds to MEA, which is an order of magnitude higher than DEA and MDEA for both N_2O and CH_4. This implies that the number of hydroxyl groups increases the solubility of N_2O in a solvent. DEA and MDEA have close numerical values of the Henry constant with MDEA higher which agrees with the above-mentioned fact that additional carbons decrease the solubility. The trend for this case corresponds to MEA>>DEA≈ MDEA. It is important to mention that for tertiary amines like MDEA no more hydrogen atoms are present in the amine group and so no chemical reaction should be expected. The results for CO_2 thus also correspond to the real solubility.

In order to compare with experimental information and test the predictive capability of our AUA potentials for alkanolamines, Henry constants of N_2O in DEA and MDEA were also calculated at 359.1K and 327.9K. The corresponding experimental values in $kPa \cdot m^3 mol^{-1}$ are 6302 and 2830 or in MPa 63.1 and 24.1 respectively[20]. As shown, although our results reproduce the experimental trend they also underestimate the Henry constants in all cases, obtaining the best predictions for MEA with absolute average deviations of 30%, 40% and 60% for MEA, DEA and MDEA respectively. Although the force field managed to correctly predict the order of magnitude of the Henry constant, such deviations are high. Since MEA is the reference molecule for the CO_2 absorption process, we decided to re-optimize the Henry constants of N_2O in MEA at 330.8K following the same procedure as for the other systems. A final value of $\epsilon_{N(MEA)-O(N2O)}/k_B$ =80.23K was obtained, this value is approximately 18% lower with respect to the obtained value using the L-B combining rules. The transferability of this new interaction parameter was tested at two different temperatues; one lower and one higher, table 2 summarizes the results. As shown, the Henry constant dependence with temperature is properly predicted and the agreement is very good with average deviations less than 9% for all the studied cases.

Force Field	H^{sim}(MPa)	H^{exp}(MPa)	T (K)
MEA-Lachet re-optimized	51.0±3	54.1	313.3
	59.0±4	63.8	330.8
	71.0±4	78.1	356.8

Table 2: Henry constants with re-optimized unlike interactions between N_2O and MEA. Specifically the modified interaction corresponds to $\epsilon_{N(MEA)-O(N2O)}$.

3.3 MEA+N_2O+H_2O ternary system

The Henry constants of the same gases were studied in a MEA aqueous solution in the NPT ensemble at 303K, and atmospheric pressure. A simulation of 1600 million MCS was performed using rigid rotations, rigid translations, configurational bias regrowths and insertions moves with position and orientation bias. Five hundred molecules (445 H_2O molecules and 55 MEA molecules) were used in total corresponding to an amine mass fraction of approximately 30% which is a typical value used in industrial absorption processes. The TIP4P/2005, Lachet *et al.* models were chosen for H_2O and N_2O since they give a better agreement for the Henry constant and, additionally, in the previous section re-optimized interactions have been obtained for this model combination.

Table 3 shows a comparison for the N_2O Henry constant predictions in MEA+H_2O using the L-B standard mixing rules as well as the re-optimized interactions for the H_2O-N_2O and MEA-N_2O systems already studied in previous sections. The results clearly indicates that the solubility of N_2O in aqueous solutions of amines is lower than in pure amine solvents. The Henry constant of CH_4 in the mixture was also calculated obtaining a value of 3948±276 MPa which is around seven times higher than the one obtained in pure MEA. At 303K the L-B combining rule overestimates the Henry constant by around 70% with respect to the experimental value. In order to numerically check the effects of the re-optimized unlike parameters, three independent simulations were performed. In particular, one simulation was performed including only the re-optimized $\epsilon_{N1(N2O)-O(H2O)}$ parameter, another one including only the $\epsilon_{O(N2O)-N(MEA)}$ parameter, and finally, one where both re-optimized interactions were considered. As can be observed, the obtained Henry constant is better predicted when the two re-optimized parameters are taking into account. If only the re-optimized cross unlike interaction $\epsilon_{N1(N2O)-O(H2O)}$ is used, the error for the Henry constant decreases to around 40%. On the other hand, if only the optimized $\epsilon_{O(N2O)-N(MEA)}$ cross interaction is used, the result is numerically close to the one obtained with the L-B mixing rules. Finally, when both optimized interactions are included at the same time, Henry constant is in very good agreement with the experimental data whith an average deviations of 7% which is much better than the 22% reported by Chen *et al.* using a combination of OPLS for MEA, Lachet *et al.* for N_2O and TIP5P for H_2O[35]. The excellent Henry constant predictions obtained for the ternary system without any refitting of the unlike interactions between MEA+H_2O might not merely be coincidence. Wang *et al.* have carried out experiments leading to determine the N_2O solubility in several alkanolamines and their aqueous solutions. They have found for the binary systems: firstly, a larger solubility for the amine implies a larger excess property of the aqueous solution and secondly, the larger the excess property the greater the polarization will be[20]. Based on this experimental result, this probably indicates from the computational point of view that when studying the N_2O solubilities in aqueous solutions of amines one of the most important unlike interaction to be considered corresponds to the one between amine and H_2O. Although more amine/H_2O systems need to be computationally studied in order to check this assumption, we have shown in previous works on amines that the AUA4 force fields are able to reproduce with very good quantitative accuracy the excess enthalpies of primary amines, e.g., *n*-butylamine-H_2O[30] for the whole composition range as well as the MEA-H_2O[9], without any additional refitting. Therefore, for the ternary system (MEA+H_2O+N_2O), the good Henry constants results can in principle be expected due to the fact both the excess properties and the intra and intermolecular hydrogen bonds are well predicted by the TIP4P/2005-AUA combination. A detailed study focused on both intramolecular and intermolecular hydrogen bond formation in pure amines and pure alkanolamines as well as its aqueous solutions at different H_2O concentration can be found elsewhere[31].

Finally, assuming the validity of the N_2O analogy it is possible to estimate the CO_2 Henry constant in the mixture from eq-3[21] at 303K. All the information needed is given in Table 1 and Table 3, equating for the H_{CO2} gives a value of 111±7 MPa. Since no chemical reaction were considered, then, it is also possible to calculate the Henry constant of CO_2 in the mixture using the re-optimized cross parameters between CO_2 and H_2O giving a numerical value of 123 MPa. As can be observed the predicted value of H_{CO2} by way of the N_2O analogy is lower than the one predicted by simulation

Cross parameters	H^{sim}(MPa)	H^{exp}(MPa)
L-B	242±14	141.6
$\epsilon_{N1(N2O)-O(H2O)}$	198±12	
$\epsilon_{N1(N2O)-N(MEA)}$	230±14	
$\epsilon_{N(MEA)-O(N2O)}$ + $\epsilon_{N1(N2O)-O(H2O)}$	151± 9	

Table 3: Henry constants of N_2O in MEA aqueous solutions at 303K. MEA mass fraction is 30%(wt). Experimental data taken from Li *et al.*[34]

which is consistent with the experimental fact that the chemical reaction increases the solubility of CO_2 in the mixture. Nevertheless, prooving the prediction capability and accuracy of such an estimation will be only possible if the involved chemical reactions are accounted for in the simulations using for instance the reactive ensemble.

$$\left[\frac{H_{CO2}}{H_{N2O}}\right]_{H2O} = \left[\frac{H_{CO2}}{H_{N2O}}\right]_{MEA+H2O} \tag{3}$$

4 Conclusions and Prospects

For the solubility of CO_2/N_2O in water it was found that the Henry constants predictions are highly overestimated. For CO_2 solubility, none of the studied force field combinations associated with the L-B mixing rule successfully predicted the experimental value. In fact, for some cases, deviations were around 100%. For all the force field combinations studied for calculating the N_2O solubility, deviations were also high but less than for CO_2. In order to improve these predictions re-optimizations of the cross interactions for each system were performed. More specifically, the $\epsilon_{C(CO2)-O(H2O)}$ cross parameter between CO_2 and H_2O and the $\epsilon_{N1(N2O)-O(H2O)}$ cross parameter between H_2O and N_2O were adjusted and gave new values of 92.64K and 60.82K respectively. These values correspond to an increment of the ϵ parameters of 8% and 23% with respect to the L-B mixing rules. Calculations using these new cross parameters significantly improved the Henry constant predictions giving a very good agreement with respect to the experimental values. These re-optimized parameters will be very useful for future works that require the N_2O analogy in aqueous systems.

In the case of the amines+N_2O and amines+CH_4 systems, several interesting behaviors were found: i) increasing the hydrocarbon chain of a linear amine decreases the Henry constant of CH_4 while the Henry constants of N_2O apparently remain the same within the error bars. ii) the N_2O Henry constants of the branched molecules *i*-butylamine and *tert*-butylamine, which are isomers of *n*-butylamine, are numerically equivalent meaning that structural changes do not have a significant effect on the physical solubility. iii) the effect of replacing the hydrogens of an amino group by methyl groups has a substantial effect which leads to lower Henry constant values. As a result, mono-functional amines follows the trend tertiary > secondary > primary with respect to the physical solubility of gases and TA has the lowest Henry constant value among all the studied molecules. iv) for primary amines, the presence of more than one amino group (i.e. the case of multifunctional amines) drastically decreases the physical solubility of the gases by an order of magnitude. Additionally, the same effect is even higher if a hydroxyl group is considered. These predicted values of CH_4 and N_2O can be considered as an initial estimate, and more experimental data will be necessary for these amines in order to determine the quantitative accuracy of the AUA4 force field used in this work.

The average deviations between experiments and simulations of the N_2O Henry constant for the ternary mixture MEA+H_2O+N_2O was 7% when the standard Lorentz-Berthelot mixing rules for the H_2O-MEA unlike interaction along with the re-optimized parameters for H_2O-CO_2 and H_2O-N_2O the binary systems were used. Interestingly, similar deviations were obtained in a previous work where excess enthalpies of MEA-H_2O were studied over the whole composition range. More studies need to be done in order to include aqueous solutions of DEA, MDEA, EDA as well as mixtures of primary, secondary and tertiary amines in aqueous solutions.

Although re-optimizing parameters is a cumbersome task, it has been shown in this work that it is possible to get an excellent accuracy in a target property by modifying unlike cross interactions without increasing the computing time. For all the studied binary and ternary systems using the standard L-B mixing rules without additional refitting appear to be limited. This finding may be due to the limitations of non-polarizable force fields which are no doubt an over simplification for these types of mixtures. Alternative recently proposed Drude polarizable force fields for H_2O[36] and CO_2[37] may be capable of overcoming these limitations. However, to the best of our knowledge, the accuracy of these models has not yet been tested in mixtures. Finally, since there is a chemical reaction between amines and CO_2, the reactive ensemble would be needed in order to be closer to the real experimental situation. Both the use of polarizable force-fields and the reactive ensemble are beyond the scope of the present work, but are interesting areas for future exploration.

5 Supporting Information

Force field parameters, and the numerical values for all the studied systems including the binary system CH_4-H_2O are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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References

[1] Kohl, A.; Nielsen, R. Gas purification, Fifth Edition *Gulf Publishing Company* Houston, Texas. **1997**.

[2] MacDowell, N.; Florin, N.; Bouchard, A.; Hallet, J.; Galindo, A.; Jackson, G.; Adjiman, C.S.; Willians, C.K.; Shah, N.; Fenell, P. An overview of CO_2 capture technologies. *Energy Environ. Sci.*, **2010**, 3, 1645-1669.

[3] D'Alessandro, D.M.; Smith, B.; Long, J.R. Carbon dioxide capture: Prospects for new materials. *Angew. Chem. Int.*, **2010**, 49, 6058-6082.

[4] Singh, P.; Niederer, J.P.M.; Verstegg, G.F. Structure and activity relationships for amine based CO_2 absorbents-I. *Int. J. Green House Gas Control*, **2007**, 1, 5-10.

[5] Singh, P.; Niederer, J.P.M.; Verstegg, G.F. Structure and activity relationships for amine based CO_2 absorbents-II. *Chem. Eng. Res. Des.*, **2009**, 87, 135-144.

[6] Singh, P.; Verstegg, G.F. Structure and activity relationships for CO_2 regeneration from aqueous amine-based solvents. *Process Saf. Environ.*, **2008**, 86, 347-359.

[7] Orozco, G.A.; Nieto-Draghi, C.; Mackie, A.D.; Lachet, V. Transferable force field for equilibrium and transport properties in linear and branched monofunctional and multifunctional amines. I. Primary amines. *J. Phys. Chem. B*, **2010**, 115, 14617-14625.

[8] Orozco, G.A.; Nieto-Draghi, C.; Mackie, A.D.; Lachet, V. Transferable force field for equilibrium and transport properties in linear, branched, and bifunctional amines II. Secondary and tertiary amines. *J. Phys. Chem. B*, **2012**, 116, 6193-6202.

[9] Orozco, G.A.; Mackie, A.D.; Lachet V. A Transferable force field for primary, secondary and tertiary alkanolamines. *J. Chem. Theory. Comput.*, **2013**, 9(4), 2097-2103.

[10] Berendsen, H.J.C.; Grigera, J.R.; Straatsma, T.P. The missing term in effective pair potentials. *J. Phys. Chem.*, **1987**, 91(24), 6269-6271.

[11] Abascal, J.F.L.; Vega, C. A general purpose model for the condensed phases of water: TIP4P/2005. *J. Chem. Phys.*, **2005**, 123, 234505-12.

[12] Harris, J.G.; Yung, K.H. Carbon dioxide's liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model. *J. Chem. Phys.* , **1995**, 99 12021-12024.

[13] Potoff, J.J.; Siepmann, J.I. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE J.*, **2001**, 47(7), 1676-1682.

[14] Moller, D.; Oprzynski, J.; Muller, A.; Fischer, J. Prediction of thermodynamic properties of fluid mixtures by molecular dynamics simulations: methane-ethane. *Mol. Phys.*, **1992**, 75(2), 363-378.

[15] Lachet, V.; Creton, B.; de Bruin, T.; Bourasseau, E.; Desbiens, N.; Wilhelmsen, O.; Hammer, M. Equilibrium and transport properties of CO_2 + N_2O and CO_2 + NO mixtures: Molecular simulation and equation of state modelling study. *Fluid Phase Equilib.*, **2012**, 322, 66-78.

[16] Ferrando, N.; Lachet V.; Teuler J.M.; Boutin A. Transferable force field for alcohols and polyalcohols. *J. Phys. Chem. B.*, **2009**, 113, 5985-5995.

[17] Ungerer, P.; Tavitian, B.; Boutin, A. *Applications of molecular simulation in the Oil and Gas Industry*; Technip: Paris 2005, p 267.

[18] Frenkel, D.; Smit, B. *Understanding molecular simulations*; Academic Press: New york 2002.

[19] Chipot, C.; Pohorille, A. *Free energy calculations*; Springer: New york 2007.

[20] Wang, Y.W.; Xu, S.; Otto, F.D.; Mather, A.E. Solubility of N_2O in alkanolamines and in mixed solvents. *Chem. Eng. J.*, **1992**, 48, 31-40.

[21] Versteeg, G.F.; Wim, P.M.; Swaalj, van M. Solubility and diffusivity of acid gases (CO_2, N_2O) in Aqueous Alkanolamine Solutions. *J. Chem. Eng. Data*, **1988**, 33, 29-34.

[22] Hartono, A.; Juliussen, O.; Svendsen, H.F. Solubility of N_2O in Aqueous solution of Diethylenetriamine. *J. Chem. Eng. Data*, **2008**, 53, 2696-2700.

[23] Browning, J. G.; Weiland, R.H. Physical solubility of carbon dioxide in aqueous alkanolamines via nitrous oxide analogy. *J. Chem. Eng. Data*, **39**, 817-822.

[24] Moultos, O.A.; Orozco, G.A.; Tsimpanogiannis, I.N.; Panagiotopoulos, A.Z.; Economou, I.G. Atomistic molecular dynamics simulations of H_2O diffsivity in liquid and supercritical CO_2. *Mol. Phys.*, **2015**, 113(17), 2805-2814.

[25] Delhommelle, J.; Millié, P. Inadequacy of the Lorentz-Berthelot combining rules for accurate predictions of equilibrium properties by molecular simulation. *Mol. Phys.*, **2001**, 99(8), 619-625.

[26] Song, W.; Rossky, P.J.; Maroncelli, M. Modeling alkane+perfluoroalkane interactions using all-atom potentials: Failure of the usual combining rules. *J. Chem. Phys.*, **2005**, 119(17), 9145-9162.

[27] Moucka, F.; Nezbeda, I. Water-methanol mixtures with non-Lorentz-Berthelot combining rules: A feasibility study. *J. Mol. Liq.*, **2011**, 159(1), 47-51.

[28] Schnabel, T.; Vrabec, J.; Hasse, H. Unlike Lennard-Jones parameters for vapor-liquid equilibria. *J. Mol. Liq.*, **2007**, 135, 170-178.

[29] Ballal, D.; Venkataraman, P.; Fouad, W.A.; Cox, K.R.; Chapman, W.G. Isolating the non-polar contributions to the intermolecular potential for water-alkane interactions. *J. Chem. Phys.*, **2014**, 141, 649051-649055.

[30] Orozco, G.A.; Nieto-Draghi, C.; Makcie A.D.; Lachet, V. Equilibrium and transport properties of primary, secondary and tertiary amines by molecular simulation. *Oil Gas Sci. Technol.- Rev. IFP.*, **2014**, 141, 833-849.

[31] Orozco, G.A.; Mackie, A.D.; Lachet V. A molecular simulation study of aqueous solutions of amines and alkanolamines: mixture properties and structural analysis. *Mol. Sim.*. **2014**, 40, 123-133.

[32] Orozco, G.A.; Economou, I.; Panagiotopoulos, A.Z. Optimization of intermolecular potential parameters for the CO2/H2O mixture. *J. Phys. Chem. B*, **2014**, 40, 123-133.

[33] Ma'mun, S.; Svendsen, H.F. Solubility of N_2Oin aqueous monoethanolamine and 2-(2-aminoetthyl-amino)ethanol solutions from 298 to 343 K. *Energy Procedia*, **2009**, 1, 837-843.

[34] Li, M.; Lai, M. Solubility and diffusivity of N_2O and CO_2 in (monethanolamine+n-methyldiethanolamine+water) and in (monoethanolamine+2-amino-2-methyl-1-propanol+water). *J. Chem. Eng. Data* **1995**, 40, 486-492.

[35] Chen, Q.; Balaji, S. P.; Ramdin, M. Gutierréz-Sevillano, J.J.; Bardow, A.; Goetheer, E. Vlugt, J.H. Validation of the CO_2/N_2O analogy using molecular Simulation. *Ind. Eng. Chem. Res.* **2014**, 53, 18081-18090.

[36] Kiss, P.T.; Baranyai, A. A systematic development of a polarizable potential of water. (2013) *J. Chem. Phys.*, **2013**, 138(20), 204507-17.

[37] Jiang, H.; Moultos O.A.; Economou I.G.; Panagiotopoulos, A.Z. Gaussian-Charge Polarizable and Non-Polarizable Models for CO2. *J. Phys. Chem. B*, **2016**, 120, 984-994.