

A Transferable Force Field for Primary, Secondary, and Tertiary Alkanolamines

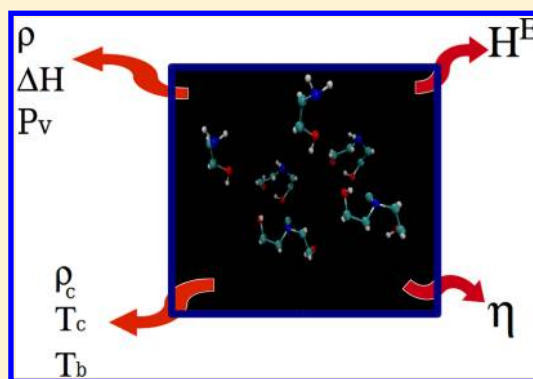
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Supporting Information

ABSTRACT: Due to the importance of alkanolamines as solvents in several industrial processes and the absence of a dedicated transferable force field for them, we have developed an anisotropic united-atom (AUA4) force field for primary, secondary, and tertiary alkanolamines. In addition to correctly reproducing the experimental densities, additional properties for six different molecules have been verified at different temperatures including vaporization enthalpies, vapor pressures, normal boiling points, critical temperatures, and critical densities. A qualitative analysis of the radial distribution function of pure monoethanolamine has also been carried out. Furthermore, the viscosity coefficients were also calculated as a function of temperature and found to be in good agreement with experimental data. Finally, and perhaps most strikingly, the prediction of the excess enthalpies of alkanolamines in aqueous solutions has been found to be in excellent qualitative agreement with experimental data.



1. INTRODUCTION

Alkanolamines play a key role as solvents in many applications including the pharmaceutical industry, sweetening gas technologies, and CO₂ capture. Despite the obvious importance of these molecules, nearly all molecular simulation studies based on force fields have focused only on monoethanolamine (MEA). In addition, these studies have combined parameters from previous force fields for amines and alcohols for the amino and hydroxyl groups with only minor refitting procedures, and the resulting properties show significant deviations from experimental data. These deviations can be expected for the short alkanolamines where the intramolecular interactions are thought to be important, and a simple combination of the amine and alcohol parameters may not be sufficient. There is thus clearly a need to develop a specific force field for this class of molecules, which should be transferable and as simple as possible while giving good quantitative predictions of the thermodynamic and dynamic properties. In addition, since alkanolamines are mostly used in aqueous solutions, it is highly relevant to study the force field performance concerning the excess enthalpy predictions of mixtures with water.

As far as MEA is concerned, previous works based on Monte Carlo (MC) or molecular dynamics (MD) simulations, have focused on a qualitative analysis of the local structure^{1–3} using a combined force field of the optimized potential for liquid simulations (OPLS) all-atom for amines⁴ with the OPLS united-atom for alcohols.⁵ In addition, da Silva et al. report deviations with experimental values of 8.5% for the liquid densities of MEA as well as 28% for vaporization enthalpies⁶ and a poor agreement with experimental data for the dilution

activity coefficients in aqueous solutions of MEA.⁷ Alejandro et al.⁸ proposed a MEA potential based on the all-atom approach. Liquid densities and surface tensions were found to have errors of 5% and 4%, respectively. Furthermore, Gubskaya et al.² have reported a rather poor agreement in the estimation of vaporization enthalpy at 333 K showing deviations of 37% compared with experimental data.

Force fields that include more than one alkanolamine are even scarcer, and to the best of our knowledge only two have been reported. In the first case, Lopez et al.⁹ proposed a force field for four alkanolamines using MD and a united-atom (UA) description for the functional groups. The force field uses an independent set of both Lennard-Jones (L-J) parameters and electrostatic partial charges for each molecule. Unfortunately, only a few points are evaluated in the properties they report, and no numerical values are given, which makes it hard to evaluate this potential. Even so, important differences with the experimental data can be easily observed from their plots, particularly for the densities of triethanolamine. Simond et al.¹⁰ also proposed an independent set of partial charges using a rescaling factor for the intramolecular interaction so as to reproduce the vaporization enthalpies at the normal boiling point and the liquid densities. Only primary alkanolamines are studied, and as for the previously mentioned works, the OPLS parameters are straightforwardly transferred, except for one OPLS L-J parameter which is adjusted in order to improve the results.

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It has been demonstrated for methylamine that the OPLS-AA force field shows significant underestimations for the liquid densities as the temperature increases above the boiling point with deviations of around 12% and 15% for the critical temperature and density, respectively.¹¹ These poor results should be expected because, just as its name suggests, this force field has been developed for liquid simulations. In addition, from our experience, a force field that presents high deviations for densities will almost certainly give poor estimates for the vapor pressures as well. Thus, together with the inaccuracies that this model already shows in liquid densities, a good behavior for vapor pressures is not expected. With regards to CO₂ capture processes using alkanolamine solutions, which have associated operating temperatures between 30 and 80 °C, a good knowledge of the thermodynamic properties including the vapor pressure is required in order to be able to control the process in an optimal manner and avoid potential solvent losses. There is thus a need for a model that is able to correctly predict these vapor pressures.

2. FORCE FIELD DETAILS

2.1. Proposed Model. As previously stated, two functional groups should be considered for alkanolamines, namely, the amino and the hydroxyl groups. For the first group, the AUA4 force field for amines will be used. The transferability of this force field has already been tested for 20 different amines including several structures, such as linear, branched, and multifunctional amines like diethylenetriamine.^{13,14} This force field has been evaluated for the prediction of liquid densities, vapor pressures, vaporization enthalpies, normal boiling points, critical densities, critical temperatures, and viscosity coefficients. For all these properties, a very good agreement has been found when compared with experimental data. In the case of the hydroxyl group, a reoptimization based on the AUA4 force field for alcohols proposed by Ferrando et al.¹⁵ will be carried out. The original force field for alcohols has been tested for diols, triols, branched alcohols, and phenols and gives an excellent accuracy for monofunctional alcohols and deviations of 5–6% in liquid density predictions for diols and triols.

Figure 1 gives a schematic representation of our proposed AUA4 model for alkanolamines using ethanolamine (MEA) as an example. As shown, two different chemical groups can be identified, namely the hydroxyl group (O–H) and the amino

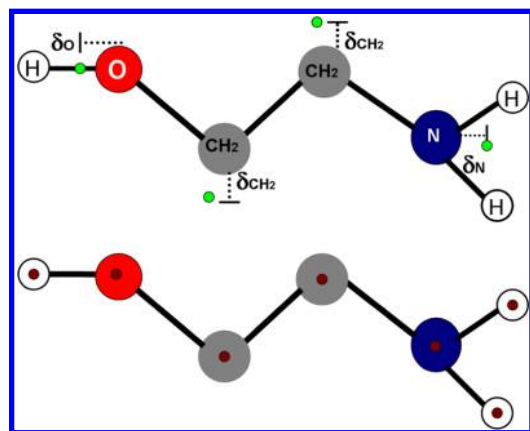


Figure 1. Schematic representation of the AUA4 force field for alkanolamines, using MEA as an example. Green circles represent the L-J force centers, whereas red circles represent the partial charges.

group (H–N–H). The AUA displacements (δ) are located following the rules reported in previous works.^{13–15} As can be seen, for this short molecule, all the atoms have an associated partial charge.

Nonbonded Interactions. Interactions between two force centers are calculated using a 6-12 L-J potential, while electrostatic interactions are calculated using Coulomb's law. Interactions between unlike force centers were calculated following the Lorentz–Berthelot combining rules.

Partial Charges and Intramolecular Energy. Unlike the aliphatic amines, where variations of dielectric constants and dipole moments from one molecule to another can be neglected,^{13,14} in the case of alkanolamines, the behavior of the dielectric constants is far more complex and such an assumption is no longer valid. The differences between molecules can be attributed to the tendency to form both intramolecular and intermolecular hydrogen bonds. Figure 2

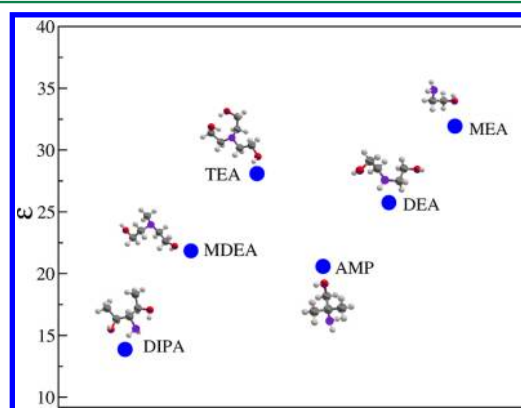


Figure 2. Dielectric constants of some alkanolamines: red represents the oxygen atom, purple the amino group, and carbon and hydrogen by gray and white, respectively. DIPA, MDEA, TEA, AMP, DEA, MEA.

shows a comparison of several experimental alkanolamine dielectric constants including primary, secondary, and tertiary alkanolamines.¹⁶ As can be observed, there are significant deviations even between the dielectric constants of the same family, for instance between primary alkanolamines MEA and 2-amino-2-methyl-1-propanol (AMP), secondary alkanolamines diethanolamine (DEA) and diisopropanolamine (DIPA), and tertiary alkanolamines methyldiethanolamine (MDEA) and triethanolamine (TEA). As a consequence, and since a unique set of partial charges is not able to properly describe the systems we are interested in, an independent set of partial charges will be proposed for each molecule.

As usual in the AUA4 force field, all bond lengths are considered to be rigid, interactions between three connected atoms are modeled using the harmonic potential given by eq 1, where k_{bend} is the bending constant, and θ and θ_0 are the bending and equilibrium bending angles, respectively.

$$U_{\text{bending}} = \frac{1}{2} k_{\text{bend}} (\cos \theta - \cos \theta_0)^2 \quad (1)$$

Interactions between four connected atoms are calculated as a function of the dihedral angle using the torsional potential given by eq 2, where χ is defined such that $\chi = \phi + 180^\circ$ and ϕ is the dihedral angle. Intramolecular electrostatic interactions are considered and calculated according to the local dipole approach proposed by Ferrando et al.¹⁵ The main advantage of

using such an approach is that it does not require additional terms, such as scaling factors. Because of the strong attraction between the amino and the hydroxyl groups, an explicit 1–4 L-J intramolecular interaction was also included.

$$U_{\text{tor}}(\chi) = \sum_{i=0}^8 c_i [\cos(\chi)]^i \quad (2)$$

The studied alkanolamines require an additional torsional potential that corresponds to $\text{OCH}_2\text{CH}_2\text{N}$. In order to calculate this potential we chose MEA as the reference molecule. The same procedure as in previous work was followed using DFT. We can add that the total energy was also computed using the second order Moller–Plesset perturbation theory (MP2) and that there were no significant differences. For the reference molecule, both L-J (including 1–4 contribution) and intramolecular electrostatic interactions were also accounted for and therefore subtracted from the total energy. The calculation of the total energy was in excellent agreement with the one reported by Chang et al.^{17,18} and Lopez et al.⁹ Note that the $\text{OCH}_2\text{CH}_2\text{N}$ torsion will be transferred for all the studied molecules.

Tables 1 and 2 summarize the L-J parameters as well as the set of partial charges proposed in this work. Bond lengths,

Table 1. Nonbonded Parameters

| force center | ϵ (K) | σ (Å) | δ (Å) | ref |
|---------------|----------------|--------------|--------------|-----------|
| CH_3 | 120.15 | 3.607 | 0.216 | 4 |
| CH_2 | 86.29 | 3.461 | 0.384 | 4 |
| CH | 50.98 | 3.363 | 0.646 | 4 |
| N(1° amine) | 137.46 | 3.415 | 0.170 | 5 |
| N(2° amine) | 120.66 | 3.172 | 0.497 | 6 |
| N(3° amine) | 47.00 | 2.600 | 0 | 6 |
| O | 125.00 | 2.930 | 0.010 | this work |

Table 2. Partial Charges (e), All of Them Proposed in This Work

| force center | MEA | DEA | MDEA | DEMEA | DIPA | AMP |
|--------------|--------|--------|--------|--------|--------|--------|
| C(O) | +0.280 | +0.265 | +0.273 | +0.260 | +0.235 | +0.255 |
| O | −0.690 | −0.700 | −0.716 | −0.690 | −0.655 | −0.680 |
| H(O) | +0.410 | +0.435 | +0.443 | +0.430 | +0.420 | +0.425 |
| C(1° amine) | +0.210 | — | — | — | — | +0.170 |
| N(1° amine) | −0.990 | — | — | — | — | −0.862 |
| H(1° amine) | +0.390 | — | — | — | — | +0.346 |
| C(2° amine) | — | +0.170 | — | — | +0.168 | — |
| N(2° amine) | — | −0.705 | — | — | −0.704 | — |
| H(2° amine) | — | +0.365 | — | — | +0.368 | — |
| C(3° amine) | — | — | +0.192 | +0.225 | — | — |
| N(3° amine) | — | — | −0.576 | −0.675 | — | — |

bending constants, bending angles, and torsional potentials were taken from previous works,^{4,12–15} except the $\text{OCH}_2\text{CH}_2\text{N}$ torsional potential that is from this work. All these numerical values can be found in the Supporting Information.

3. SIMULATION DETAILS

MC Simulations. The Gibbs ensemble MC method at constant volume and temperature was used to calculate the liquid–vapor equilibrium properties of the different alkanolamines. In most cases, 120 million MC steps (MCS) with an equilibration of 10 million MCS were used, where one step corresponds to a simple MC move. Periodic boundary conditions and the minimum image convention were applied. A spherical cutoff equal to half of the simulation box was used to calculate the L-J interactions between force centers, and the Ewald procedure was applied to handle the long-range electrostatic interactions¹⁹ with a maximum of 7 vectors for each direction of the reciprocal space and a scaling parameter $\alpha = 2$ in reduced units. A total of 350 molecules were used for the simulations, except for temperatures close to the critical point where we increased the size of the system up to 600 molecules. The following MC moves were used: translation (20%), rigid rotation (20%), configurational bias regrowth (20%), transfer with insertion bias (39.5%), and volume change (0.5%). The amplitudes of translations, rotations, and volume changes were adjusted during the simulation to achieve an acceptance ratio of 40% for these moves. The critical coordinates (critical density ρ_c and temperature T_c) were calculated through a scaling law with a critical exponent β fixed to 0.325 and the law of rectilinear diameters.¹⁹ Normal boiling points (T_b) were estimated by fitting the vapor pressure (P_v) to the Clausius–Clapeyron equation at different temperatures. The simulations were performed using the in-house GIBBS MC code developed by IFPEN and Orsay University.¹²

Molecular Dynamics. The equations of motion were integrated using the velocity Verlet algorithm with constrained bonds using the Rattle algorithm.²⁰ The simulations were performed in the NPT ensemble using both the Berendsen barostat and thermostat. The Ewald procedure was also applied to handle the long-range electrostatic interactions. Equilibration runs of 1 ns were used, while for the production part, 5 ns was applied. In both cases, the integration time step was 2 fs. A Verlet nearest-neighbor list was also included in order to improve the performance of the simulations. In all cases, 250 molecules were placed in a cubic box with periodic boundary conditions. To estimate the viscosity coefficients, we used the Green–Kubo formalism. Calculations were performed using the Newton code developed at Orsay University.

Excess Enthalpies. Excess enthalpies were calculated by MC simulations in the NPT ensemble. Three different systems were studied, namely, MEA + water at 298 K, DEA + water at 313 K, and MDEA + water at 298 K. The same moves as those already mentioned for the Gibbs ensemble calculations were chosen, with the exception of the transfer move. A total of 300 molecules for each system was used, with simulations of up to 250 million MCS. The TIP4P/2005 potential was chosen for the water model.²¹ The excess enthalpies, H^E , for a binary system were calculated at each mixture composition by means of eq 3:

$$H^E = H - x_1 H_1 - (1 - x_1) H_2 \quad (3)$$

with H the enthalpy defined as

$$H = U_{\text{ext}} + U_{\text{int}} + K + PV \quad (4)$$

where U_{ext} is the intermolecular potential energy, U_{int} the internal potential energy, and K , P , V are the total kinetic energy, pressure, and volume of the system, respectively. H_i is

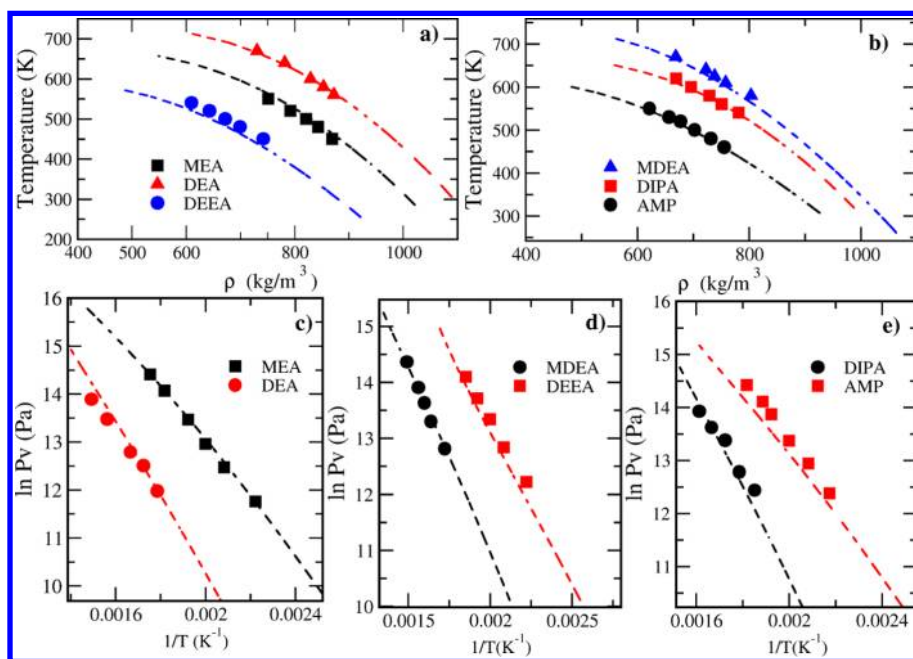


Figure 3. Comparison between experimental and AUA4 force field predictions of liquid densities (ρ_L) and vapor pressures (P_v). In all cases, the dashed lines correspond to the DIPPR experimental correlations²² except for vapor pressures of DIPA, DEEA, and AMP which are based on DIPPR predictions by means of the Racket equation.

the enthalpy of the pure component i and x_i the molar fraction of component 1. We assume that the kinetic energy of the mixture can be obtained from the molar average of the pure component contributions. Thus, two independent simulations need to be carried out in order to estimate the configurational enthalpies for the pure components H_1 and H_2 . Then, at a fixed composition of the binary mixture, the total configurational enthalpy H can be determined, and therefore the corresponding excess enthalpy is calculated from eq 3. For both mixtures, 9 different molar compositions were used ranging between 0.1 and 0.9 with steps of 0.1.

4. RESULTS

4.1. Optimization. Before proceeding to the reoptimization of the hydroxyl group, we studied the AUA4 force field performance using the original parameters for the two AUA4 functional groups on MEA. Simulations were done at four different temperatures in the NVT Gibbs ensemble. As a result we obtained global average deviations of 5% in liquid densities (ρ_L), 7% in vaporization enthalpies (ΔH), and 45% in vapor pressures (P_v). Compared with the previously mentioned works in the introduction where MEA has been studied, it is possible to conclude that the results in vaporization enthalpies and liquid densities are even better than the ones reported when the OPLS force field is used (note that vapor pressures are not reported in previous works). Nevertheless, in our opinion, deviations of 45% for the vapor pressure are very high, and deviations of 5% in densities also represent a large difference and need to be improved.

The deviations obtained suggest that, at least for short alkanolamines where intramolecular interactions are not negligible, the transferability of the potential can not be done straightforwardly, and a force field reparametrization is needed. In order to confirm this assumption, the performance of the force field was also checked for a long alkanolamine where both functional groups have a larger separation; this means that

intramolecular electrostatic interactions are smaller and therefore the polarization effect may not be important. This is the case of 6-amino-1-hexanol, where the functional groups are separated by four carbons. Unfortunately, for long-chain alkanolamines there is a scarcity of experimental information for quantitative thermodynamics properties, such as densities, vaporization enthalpies, etc. Nevertheless, experimental information is available with regards to the normal boiling point. Thus, using the simulation results obtained at different temperatures, the normal boiling point was calculated using the Clausius–Clapeyron equation. As a result, we obtained a normal boiling point of 492 ± 2 K compared with the experimental value²² which is reported to be between 496 and 500 K. This excellent agreement supports the above-mentioned hypothesis. We should remark that the normal boiling point is not included in the AUA4 force field parametrization and hence demonstrates the capability of the force field to make predictions.

Typical industrial applications use alkanolamines that have the two functional groups at a short distance, so that a reoptimization of the potential should be undertaken. As has already been mentioned, we chose to perform a reoptimization of the oxygen belonging to the hydroxyl group. The main goal was to modify as little as possible the original parameters proposed by the AUA4 force field for alcohols. A study for these systems of the influence of changing the L-J parameters (σ , ϵ , and δ) showed that the highest sensibility was found for sigma. Thus a reoptimization was done based on this information. To carry out the optimization, three molecules were selected, namely MEA, DEA, and MDEA. This training set was chosen since it includes the key features of all alkanolamines, i.e., primary, secondary and tertiary alkanolamines at the same time. It should be noted that proposing an individual set of L-J parameters for each molecule implies a loss of transferability for the force field, and one of the key objectives of this work is to develop a potential that can be

applied reliably to any alkanolamine. We therefore have transferred the same reoptimized L-J AUA parameters for all of the studied alkanolamines. The optimization procedure proposed by Bourasseau et al. was used and details of this procedure can be found in the literature.^{13,14,23}

4.2. Thermodynamic Properties. In addition to studying the behavior of the training set (MEA, DEA, MDEA) at different temperatures, we have also included property calculations for the following alkanolamines: DIPA as a secondary branched alkanolamine, AMP as a primary hindered alkanolamine, and diethylaminoethanol (DEEA) as a tertiary alkanolamine. Note that these molecules are different in terms of chemical structure and so represent a good set to study the force field transferability. Figure 3 shows a comparison between the results obtained using the AUA4 force field for alkanolamines and experimental data^{22,24} for liquid densities (ρ_L) and vapor pressures (P_v). As can be inferred from Figure 3, the agreement is very good. Vaporization enthalpies (ΔH) were also studied, however since reliable experimental information was found only for MEA, this property is not shown. The numerical values showing the behavior of this property for all the studied molecules can be found in the Supporting Information. All the experimental data were taken from the DIPPR database,²² and the vapor pressures for DIPA, DEEA and AMP correspond to predictions of the DIPPR database with associated uncertainties of 25%, 25%, and 10%, respectively.

In short, and only for the molecules where experimental information is available, we have obtained a global absolute average deviation (AAD = $|X^{\text{exp}} - X^{\text{sim}}|/X^{\text{exp}}$) of 1.0% for ρ_L , 6.4% for P_v , and 2.3% for ΔH . These results confirm the capability of the force field to correctly predict the properties of molecules that do not belong to the training set. The numerical values for all the studied properties and molecules can be found in the Supporting Information.

4.3. Normal Boiling Points and Critical Points. Table 3 gives the critical coordinates and normal boiling points. As

Table 3. Critical Temperatures and Densities and Normal Boiling Points, Comparison between the Experimental or Predicted Values and the AUA4 Force Field Predictions^a

| molecule | T_c (K) | | ρ_c (kg/m ³) | | T_b (K) | |
|----------|--------------------------------|-------------------|--------------------------------|-------------------|---------------------|------------------|
| | exp | sim | exp | sim | exp | sim |
| MEA | 678 ₃₃ | 679 ₄ | 319 ₁₈ ^c | 315 ₅ | 443.2 ₄ | 442 ₂ |
| DEA | 768 ₂₃ | 778 ₈ | 303 ₁₇ ^c | 296 ₅ | 541.5 ₁₅ | 535 ₃ |
| MDEA | 742 ₁₀ ^c | 739 ₁₀ | 304 ₁₃ ^c | 325 ₁₀ | 520.7 ₅ | 523 ₂ |
| DIPA | 724 ₂₅ ^b | 727 ₆ | 298 ₁₃ ^c | 311 ₁₀ | 521.9 ₅ | 501 ₅ |
| AMP | 620 ₃₁ ^c | 616 ₆ | 283 ₇₀ ^c | 305 ₁₀ | 438.7 ₄ | 430 ₆ |
| DEEA | 592 ₃₀ ^c | 610 ₆ | 292 ₇₂ ^c | 297 ₁₀ | 436.1 ₄ | 417 ₆ |

^a T_c = critical temperature; ρ_c = critical density; and T_b = normal boiling point. ^bValue taken from the NIST database. ^cPredicted values taken from DIPPR by the method of Lydersen. The subscripts give the statistical uncertainties of the last digit(s).

shown, the numerical results are in good agreement with the experimental values taking the error bars into account. Furthermore, our force field is able to predict several experimental features: (i) as the number of hydroxyl groups increases, e.g. MEA to DEA, the critical temperature and normal boiling point increase as well; (ii) there is only a slight numerical difference in the evaluated properties between DEA and MDEA, which are secondary and tertiary alkanolamines;

and (iii) both AMP and MEA are primary alkanolamines, however AMP is branched, and the critical temperature of AMP is significantly lower than MEA, but the normal boiling points are close; the same behavior is also correctly reproduced for DEA and DIPA.

4.4. Radial Distribution Function of MEA. In order to study the structure of the liquid phase of pure MEA, we have performed a simulation in the NPT ensemble at 298 K and 1 atm. Figure 4a–c shows the obtained radial distribution

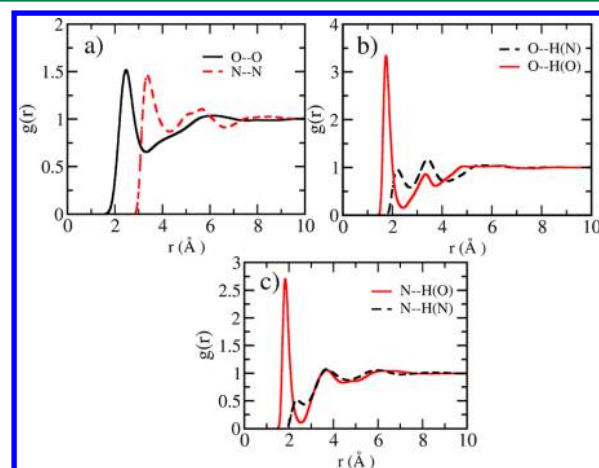


Figure 4. Intermolecular radial distribution functions for MEA from the AUA4 force field of this work.

functions ($g(r)$) as a function of the interatomic distances for some of the atoms, namely, O, N, H(N) and H(O). To the best of our knowledge, no experimental information is available for the structure of MEA in the liquid phase. Nevertheless, the liquid structure of MEA has been widely studied by molecular simulation, so that a comparison of our results with previous works can be established.

Figure 4a, corresponds to the oxygen–oxygen and nitrogen–nitrogen intermolecular radial distribution functions ($g_{(O-O)}$, $g_{(N-N)}$). As shown, both functions present a first sharp peak located at 2.3 and 3.3 Å, respectively. In both cases, it is also possible to identify a second less well-defined peak around 5.7 Å that might be related to the neighbors located in a second shell. From Figure 4b,c, an important difference between the hydrogens of the hydroxyl group H(O) and the hydrogens belonging to the amino group H(N) can be observed. A well-defined sharp peak is found for H(O) with both the nitrogen or the oxygen force centers but with slightly different amplitudes. The first peak in both cases is located at 1.8 Å and is probably related with the presence of a hydrogen bond. For the second case (H(N)), the peaks are significantly smaller which might indicate that the hydrogen bonds in MEA are related with the hydrogens belonging to the hydroxyl group. These results are in good qualitative agreement with previous MEA works,^{1,6,8} particularly with the peak positions reported by Gubskaya et al. who have used a modified OPLS force field by means of 1–4 rescaling factors.²

4.5. Excess Enthalpies. Since alkanolamines are mostly used as aqueous solutions in CO₂ capture processes and sweetening gas technologies, the performance of the force field for predicting excess enthalpies in aqueous solutions is highly relevant. Several nonpolarizable force fields for water have been recently revised in a review by Vega and co-workers^{2,5} where different properties, such as dielectric constants, melting

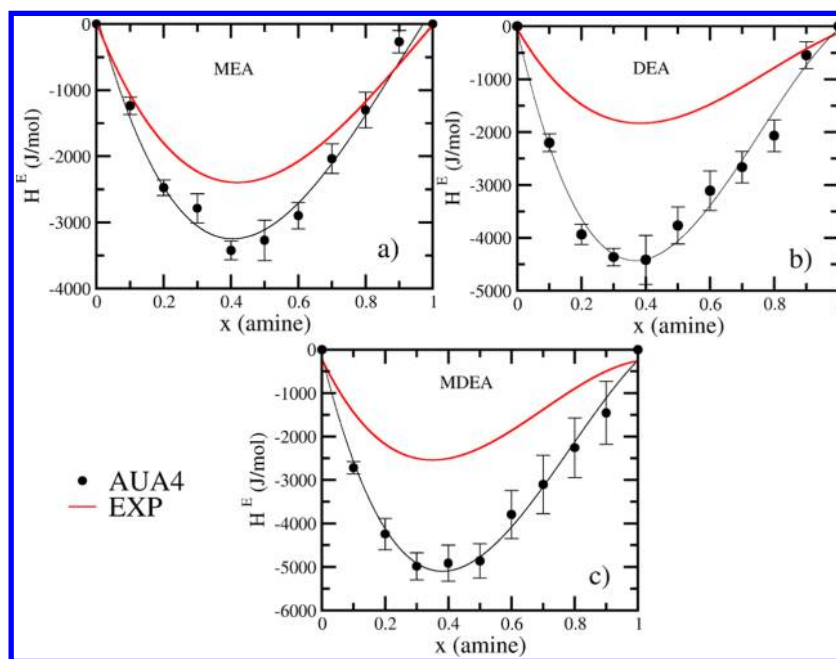


Figure 5. Excess enthalpies of several alkanolamines + water: (a) MEA + water (298 K); (b) DEA + water (313 K); and (c) MDEA + water (298 K). Experimental values correspond to the red line, and AUA4 predictions correspond to the black filled circles. The continuous black line is used merely as a guide for the eye.

properties, phase equilibrium diagrams among others, were calculated. They found that on average the TIP4P/2005 model²¹ best reproduces the water behavior for all these properties. Consequently, in this work this model was chosen for our simulations. We would like to emphasize that in the following mixture simulations, the force fields have not been modified in any way and have been straightforwardly applied using the standard Lorentz–Berthelot mixing rules for the cross interactions.

Figure 5 shows both the experimental values^{26–28} as well as the AUA4 force field simulation results for three alkanolamines. From the experimental data it is possible to observe that MDEA has slightly larger excess enthalpies with the minimum point located around $x(\text{amine}) = 0.3$, followed by MEA whose H^E magnitudes are close to MDEA but with the minimum located around $x(\text{amine}) = 0.4$. Finally, DEA has the smallest enthalpies and the minimum located between 0.3 and 0.4. Although the force field overestimates the excess enthalpies, in all cases it is able to properly reproduce both the correct sign and trend, including the positions of the minima. In addition for MEA, the numerical predictions are even in good quantitative agreement with the experimental values. These results are particularly encouraging in the sense that, first, the excess properties represent the nonideal behavior of a mixture and so determining such a property is a challenge from a computational point of view and, second, considering the fact that no additional refitting was required for the mixture interactions, even predicting the correct sign can be difficult.

4.6. Viscosity Coefficients. The viscosity coefficients for pure MEA, DEA, and MDEA were calculated as a function of temperature. Four different and independent initial configurations were used. The values presented here correspond to the average of the results obtained for these four independent simulations and their corresponding standard deviations. Figure 6 shows a comparison between the experimental (black filled circles) and simulated (gray filled circles) viscosity coefficients

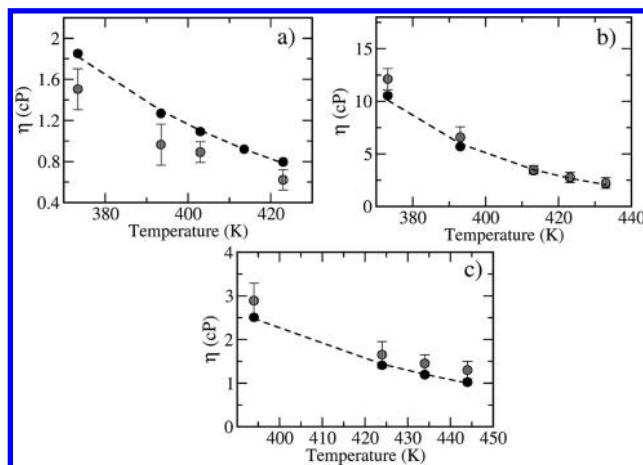


Figure 6. Shear viscosity as a function of temperature: (a) MEA; (b) DEA; and (c) MDEA. Black and gray filled circles correspond to the experimental and simulated values, respectively. The dashed line is used merely as a guide for the eye.

at different temperatures. From an experimental point of view, the behavior of the viscosities of alkanolamines is interesting in the sense that although DEA (secondary alkanolamine) is much more viscous than MDEA (tertiary alkanolamine), MDEA is only slightly more viscous than MEA (primary alkanolamine), i.e., the viscosity trend is $\text{DEA} \gg \text{MDEA} > \text{MEA}$. As can be observed from Figure 6, the AUA4 force field is able to correctly reproduce this trend. The highest deviations with experiment were found for MEA, where an average deviation of 21% was found. For secondary and tertiary alkanolamines, the predictions are in very good agreement with the experimental results^{22,29,30} with deviations for DEA and MDEA of 8% and 7%, respectively.

5. CONCLUSIONS AND PROSPECTS

We have presented the results of a new AUA4 force field for alkanolamines. A range of different properties has been validated against experimental data for several primary, secondary, and tertiary alkanolamines. These results, and particularly the good agreement with experiment for the excess enthalpies of mixing, motivate us to apply the force field in future works. In particular, we plan to calculate thermophysical properties, such as the Henry constants or diffusion coefficients of green house gases like CO₂ or N₂O in aqueous solutions of alkanolamines, which are necessary for the design of novel processes and the optimization of present ones.

■ ASSOCIATED CONTENT

● Supporting Information

Force field parameters and numerical values for the studied thermodynamic properties are presented. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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