



Predictions of fluidities of amines by molecular simulations: TraPPE-EH vs. OPLS-AA

Alejandra Rendón-Calle ^a, Gustavo A. Orozco ^{b,*}, Santiago Builes ^{a,**}

^a Dpto. Ingeniería de Procesos, Universidad EAFIT, Carrera 49 No 7 sur-50, 050022, Medellín, Colombia

^b Facultad de Ciencias, Dpto. de Física, Universidad Antonio Nariño, Carrera 3 Este No 47 A-15, 110211, Bogotá, Colombia

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ABSTRACT

Amines have several important industrial properties and commercial applications, such as gas sweetening and carbon capture; and the synthesis of: tranquilizers, decongestants, and azo dyes. For the design of many engineering applications, it is important to calculate the density and viscosity of the substances in order to determine how the fluids should be handled, stored, and discarded. In this work, the accuracy of two common force fields for amines, TraPPE-EH and OPLS-AA, was evaluated with respect to their predictions of liquid densities and fluidities for a large set of amine molecules including primary, secondary and tertiary. We propose the use of the reciprocal of viscosity, the fluidity, as a more accurate assessment of the predictions of viscosity at different temperatures. The fluidity was calculated using molecular dynamics in the isothermal-isobaric ensemble (NPT) along with the Green Kubo formalism. The simulation results were compared to available experimental information in order to provide a quantitative study of the force fields accuracy as well as their transferability to amines and thermodynamic conditions different to the ones used in their original parametrization. Overall, liquid densities and fluidities are well reproduced by the TraPPE-EH force field with absolute average deviations of 1.5% and 12%, respectively. However, important deviations were found for the OPLS-AA force field corresponding to 3.6% and 28% for density and fluidity respectively. In order to obtain better estimations of the fluidity, a temperature correction that accounts for the error in the liquid density predictions was proposed. Once the temperature correction was included the average deviation of the fluidity decreased to 10% for TraPPE-EH and to 18% for OPLS-AA.

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1. Introduction

Earth's temperature is the result of the balance between the energy entering and leaving the atmosphere. The energy leaving the atmosphere is regulated by the natural greenhouse effect, which raises Earth's surface temperature. The concentration of greenhouse gases has allowed a regulated climate and the existence of living ecosystems. However, Earth's atmospheric conditions can vary over time, causing climate changes. Nowadays, climate change is an evident phenomenon where the average global temperature has gradually increased since the beginning of the 20th century. Carbon dioxide (CO₂) is one of the main

contributors to this climate change.

In order to mitigate carbon dioxide emissions, a vast number of technologies are being explored. Processes, such as chemical absorption [1], physical absorption [2], adsorption in porous materials [3,4], membrane separation [5], cryogenic distillation [6] and biotechnological processes [7] have been explored extensively for the separation of carbon dioxide. Nevertheless, the most mature and readily applied technology for the separation of CO₂ is chemical absorption/desorption using aqueous amine solutions [8].

The performance of amine solvents in absorption and desorption columns is influenced by their physical properties. Properties such as density and viscosity are required in thermal and hydraulic calculations [9]. They are critical in process design because they determine how the fluids should be handled, stored, and discarded. For instance, amine viscosity has a direct effect on heat transfer coefficients, which are required in the design of heat exchangers and stripper columns. Viscosity also has a direct effect on pressure drops, which are required for pumping and piping calculations [10].

* Corresponding author.

** Corresponding author.

E-mail addresses: gustavo.orozco@uan.edu.co (G.A. Orozco), sbuiles@eafit.edu.co (S. Builes).

Moreover, density and viscosity are essential for calculating physicochemical properties such as reaction rate constants, solubility and diffusivity.

Therefore, reliable and accurate thermodynamic data for amines covering a wide range of temperatures, pressures and compositions are required to improve existing designs for CO₂ capture. Most common fluid property models in process design and optimization are equations of state or Gibbs free energy models, which generally require parametrization to experimental data. However, experimental data are often not available or might be difficult to obtain for the specific systems under study [11].

Molecular simulations allow to estimate transport and thermodynamic properties requiring only a limited set of experimental data to parametrize. Usually, the development of a force field for a chemical family of molecules is based on fitting of either (i) experimental data of a given set of properties or (ii) theoretical predictions from ab-initio calculations. In both cases a relatively small number of molecules is used for the training set, which is considered to be able to provide accurate parameters for the entire family of molecules.

There are few interaction potentials available in the literature for the calculation of properties of amines using molecular simulations. Rizzo and Jorgensen [12], following the Optimized Potentials for Liquid Simulations all atom (OPLS-AA) philosophy, developed parameters for primary, secondary and tertiary amines. They reported the liquid density and vaporization enthalpy at one temperature, obtaining good agreement with the experimental data. Wick et al. [13], following the Transferable Potentials for Phase Equilibria Explicit Hydrogens (TraPPE-EH) philosophy, proposed another all-atom approach to study amines. Six different amines were considered, including primary, secondary and tertiary amines. Although the available experimental data for the fitting was scarce, good agreement was obtained for the prediction of the critical temperature and saturated liquid densities. The most comprehensive study of amines to date has been performed by Orozco et al. [14–17]. They developed parameters for primary, secondary and tertiary amines, including polyamines, based on the Anisotropic United Atom (AUA) approach. Their study included more than 20 different amine molecules and several properties such as liquid densities, vapor pressures, vaporization enthalpies, normal boiling points, critical densities, and excess properties. They also estimated shear viscosities for 13 amines. They found an average deviation with the experimental data of 2% in the densities and 11% in the viscosities. Baskaya et al. [18] developed a transferable force field for amines using a discontinuous potential, where the interactions were considered constant in 4 different steps of diminishing depth [19]. They reported the vapor pressures and liquid densities of 11 amines, including primary and secondary amines. The deviations were around 13 and 4% for the vapor pressure and the liquid density, respectively. Moreover, the liquid density errors increased significantly with the chain length, in particular for chains larger than pentylamine. Patel and Brooks [20] implemented a fluctuating charge force field for amines adjusting the liquid phase density and enthalpy of vaporization of methylamine. Bael and Patel [21] studied the extensibility of this force field by calculating the liquid densities, enthalpies of vaporization, isothermal compressibilities, isobaric heat capacities and self-diffusion coefficients for methylamine, ethylamine and propylamine. The deviations of the predicted results were around 3% for the liquid density, however the error increased with the molecule size.

Salomon et al. [22] adjusted the TraPPE-EH force field for the polyamines hexamethylenediamine and diethylenetriamine. They found that the liquid phase densities calculated at 298 K agreed within 3% with the experimental results and that the viscosity of the mixture of these amines and CO₂ had a qualitative agreement

with the experimental results.

Although the AUA force field has shown to accurately predict amine properties, the non-straightforward implementation of the anisotropic force field in the most commonly used open source molecular dynamics codes like Gromacs, LAMMPS and DL_POLY has not allowed its widespread use. In this work the most commonly used amine force fields (TraPPE-EH and OPLS-AA) are compared in order to determine their accuracy for the prediction of viscosities and densities at five different temperatures [23]. The equilibrium properties of amine molecules calculated by these widely used force fields, to the best of our knowledge, have not been critically evaluated on a large number of molecules. Additionally, predictions of transport properties of amines using these potentials has not been explored yet. A systematic study of these properties could help the future establishment of molecular simulation as a mainstream tool for chemical process design, in particular for the design of CO₂ adsorption/desorption processes.

The widespread usage of molecular simulations as a general tool for the calculation of thermodynamic and transport properties in engineering applications requires critical validation of the force fields [24]. Coleman et al. [25] performed molecular dynamics simulations of 146 organic liquids using OPLS-AA and GAFF force fields to evaluate densities, enthalpies of vaporization, surface tension, heat capacity at constant volume, thermal compressibility and volumetric expansion coefficients. They established an online database for the properties of the studied substances and found very good agreement for the prediction of densities in OPLS-AA. However, Zubillaga et al. found that the surface tensions reported in this database were not correct because a small truncation distance was used [26].

The objective of this work is to study the accuracy of both OPLS-AA and TraPPE-EH force fields on a large set of molecules, consisting of primary, secondary, tertiary and bifunctional amines. In order to determine the force field that best describes the studied properties a total of 19 amines were studied and compared to available experimental information. The shear viscosity and liquid densities are evaluated using molecular dynamics in the isothermal-isobaric ensemble (NPT). For all cases the Green-Kubo formalism is used for calculating the shear viscosity coefficients of pure amine molecules [27].

2. Methods

2.1. Molecules and force fields

As aforementioned 19 different amines were studied in this work. Namely, six primary amines, five secondary amines, six tertiary amines and two bifunctional primary amines. Fig. 1 shows the chemical structure and the abbreviations used for the studied set.

OPLS-AA and TraPPE-EH force field parameters were taken from the works of Rizzo et al. [12] and Wick et al. [13] respectively. Briefly, OPLS-AA force field considers: geometric mixing rules, bond stretching and bending angles represented through a harmonic potential and torsional angle interactions using a cosine series expansion. Intramolecular interactions of atoms separated by three bonds are scaled by a factor of 0.5 for both Coulombic and LJ interactions, and atoms separated by more than three bonds do not considered scaling factors. The TraPPE-EH force field considers: the Lorentz-Berthelot mixing rules and rigid bonds. Bending angles are also calculated using a harmonic potential and torsional angle interactions are the same proposed by the OPLS-AA force field.

2.2. Simulation details

Simulations were performed at 5 different relative

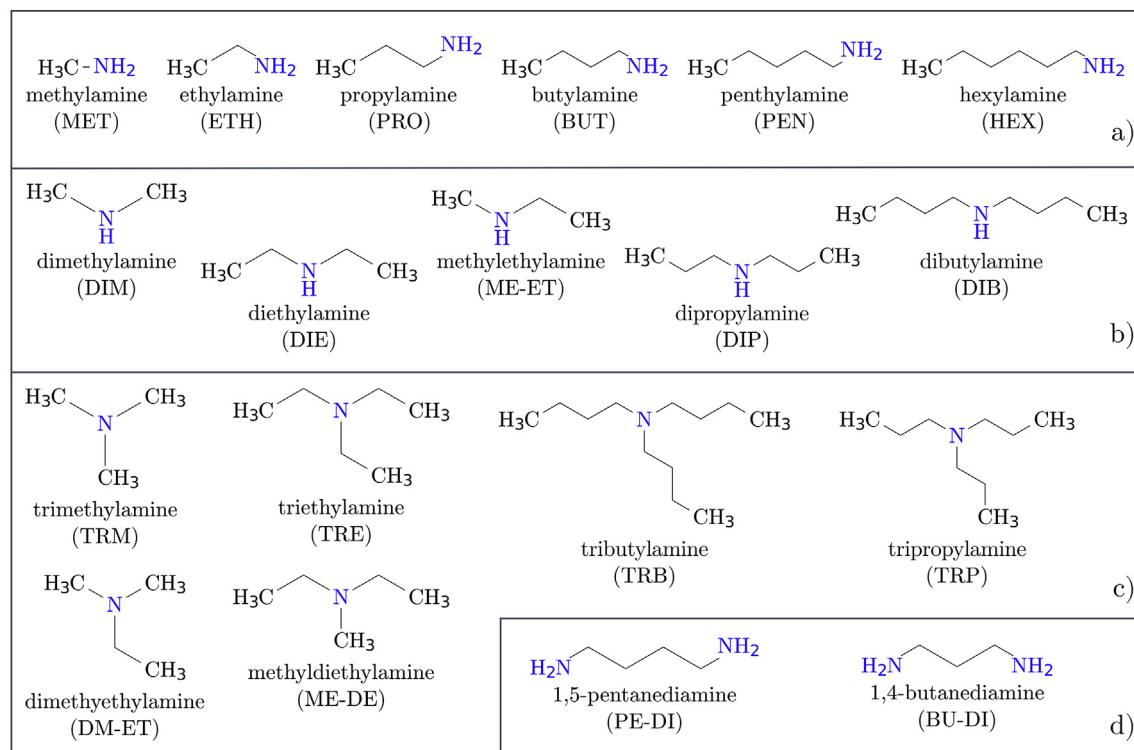


Fig. 1. Molecular structures of the studied amines (A) primary, (B) secondary, (C) tertiary, and (D) bifunctional.

temperatures, namely, 0.75, 0.80, 0.85, 0.90 and 0.95 times the saturation temperature of each molecule at 100 kPa. These relative temperatures were used instead of absolute temperatures for comparison among the different molecules at similar thermodynamic states. For all simulations, 343 molecules were initially placed in a simulation box with a face-centered cubic (FCC) symmetry under periodic boundary conditions. Molecular dynamics simulations were performed using GROMACS V5.1 [28–30]. Two equilibration runs were carried out, the first one in the canonical NVT ensemble during 100 ps with an integration time step of 1 fs, and the second run was performed in the NPT ensemble during 1 ns with a time step of 2 fs and 100 kPa. Production runs were performed in the NPT ensemble for 15 ns with a time step of 2 fs using the Nose-Hoover thermostat with a time constant for coupling of 10 ps and the Parrinello-Raman barostat at 100 kPa, with compressibility set to $4.5 \times 10^{-5} \text{ bar}^{-1}$ and a time constant of 5 ps. The cut-off radius for the LJ and the real space electrostatic interactions were fixed to 12 Å and 14 Å for OPLS-AA and TraPPE-EH, respectively. Long range corrections for energy and pressure were also applied. Particle mesh Ewald was used to compute the long-range electrostatic interactions, with a Fourier spacing equal to 0.1 nm and a tolerance of 1×10^{-5} .

The TraPPE-EH force field was originally parametrized using rigid bonds, therefore the LINCS algorithm was used to constrain all bonds. On the other hand, the OPLS-AA force field parametrization considers fully flexible molecules, and therefore no additional constraints were employed.

For each temperature, four independent simulations of equilibration and production runs were computed in order to assess the intrinsic errors of the calculations. Hence, the values presented here correspond to the average of the obtained viscosities for the four configurations with the corresponding standard errors reported in the [Supplementary Material](#).

The shear viscosity coefficient was calculated using the Green-

Kubo formalism, which relates the shear viscosity (η) to the time correlation functions [27].

$$\eta = \frac{\langle V \rangle}{k_B T} \int_0^t \langle \sum_{ij} P_{ij}(t - t_0) P_{ij}(t_0) \rangle dt \quad (1)$$

Where k_B is the Boltzmann constant, T is the temperature of the system, and $\langle V \rangle$ the average volume of the simulation box. Angle brackets denote an ensemble average over all time origins t_0 . In order to improve the statistics, the auto-correlation function was averaged over all independent off-diagonal tensor elements P_{xy} , P_{yz} and P_{zx} . The terms $(P_{xx} - P_{yy})/2$, and $(P_{yy} - P_{zz})/2$ were also included due to the rotational invariance of the molecule. The auto correlation functions were calculated from these stress components, which were stored every 2fs, considering all configurations as a time origin.

3. Results and discussion

3.1. Densities

The density (ρ) in each simulation was calculated from the constant mass (M) of the system divided by the average volume ($\langle V \rangle$):

$$\rho = \frac{M}{\langle V \rangle} \quad (2)$$

Experimental data were obtained from a correlation of saturated liquid density as a function of temperature, using the modified form of the Rackett equation [31,32].

$$\rho = AB^{-\left(1 - \frac{T}{T_c}\right)^n} \quad (3)$$

Where A , B , and n are regression coefficients; T is the temperature and T_c is the critical temperature. This model predicts accurately the variation of the saturated liquid densities over the entire temperature range with an average error of 0.4% [31,33].

Although the simulations were performed at constant 100 kPa of pressure instead of saturation conditions, the comparison is performed against saturated liquid densities due to higher availability of experimental data at those conditions. However, it is expected that the results are similar due to the low compressibilities of liquids and the low pressures under consideration.

The absolute average deviation (AAD) was defined as the absolute difference between experimental and simulated values divided by the experimental data ($AAD = |x_{exp} - x_{sim}|/x_{exp}$). The AAD in density was 1.3% for TraPPE-EH (1.4%, 1.2% and 1.2% for primary, secondary and tertiary amines, respectively) and 3.6% for OPLS-AA (3.1%, 4.2% and 3.2% for primary, secondary and tertiary amines, respectively). Results for the whole set of molecules are available as Supplementary Material.

Fig. 2 shows a comparison between the simulated and the experimental densities for all the studied amines including both TraPPE-EH and OPLS-AA force fields, the AUA values reported by previous studies are also included. Although the overall AAD was low for both force fields, this value was not constant for either force field. Changes in temperature show differences in the predicted density trend. For instance, in TraPPE-EH, MET shows a larger deviation at low temperatures (1.5%) than at high temperatures (1.0%), whereas molecules such as HEX show the opposite trend (increasing from 1.2 to 2.6%). OPLS-AA exhibited much larger variations (decreasing from 5.2 to 1.6% for MET) and the largest deviations were mostly observed at the lowest temperatures (decreasing from 3.0 to 0.6% for HEX). These differences in the prediction of densities at low temperatures may have a notorious effect on properties such as viscosity where a substantial increase is observed by decreasing the temperature.

OPLS-AA presents in general an overprediction of the experimental data, this behavior is in agreement with the data reported by van der Spoel et al. [28] for amines. This trend decreases with temperature and might be due to the way the parameters for OPLS-AA were fitted for densities at a single fixed temperature. The largest errors for OPLS-AA are found for diamines, which were not explicitly considered in the parametrization. TraPPE-EH and AUA present excellent agreement to experimental densities for all the studied molecules at different temperatures. Despite the fact that diamines were not considered in the parametrization of the TraPPE-EH force field, liquid densities predictions of butanedi-amine and pentanedi-amine are in very good agreement with the experimental values.

3.2. Viscosities

As pointed out by Baskaya et al. [18], the lack of liquid phase experimental data has hindered the development of force fields for other functional groups in the same manner they were developed for alkanes. Available experimental data for the transport properties of pure liquid amines is still scarce and present an intrinsic error due to all the uncontrollable variables interfering with the experiments.

This lack of experimental data requires an interpolation of available data in order to calculate the AAD for the simulated temperatures. For the amines considered in this work, a parametrization of the temperature dependence of the viscosity (η) was performed based on available experimental data of viscosities [34–36]. The viscosity of each amine was parametrized to the non-linear regression given by equation (4), which has been proposed for correlating viscosities of different substances [37].

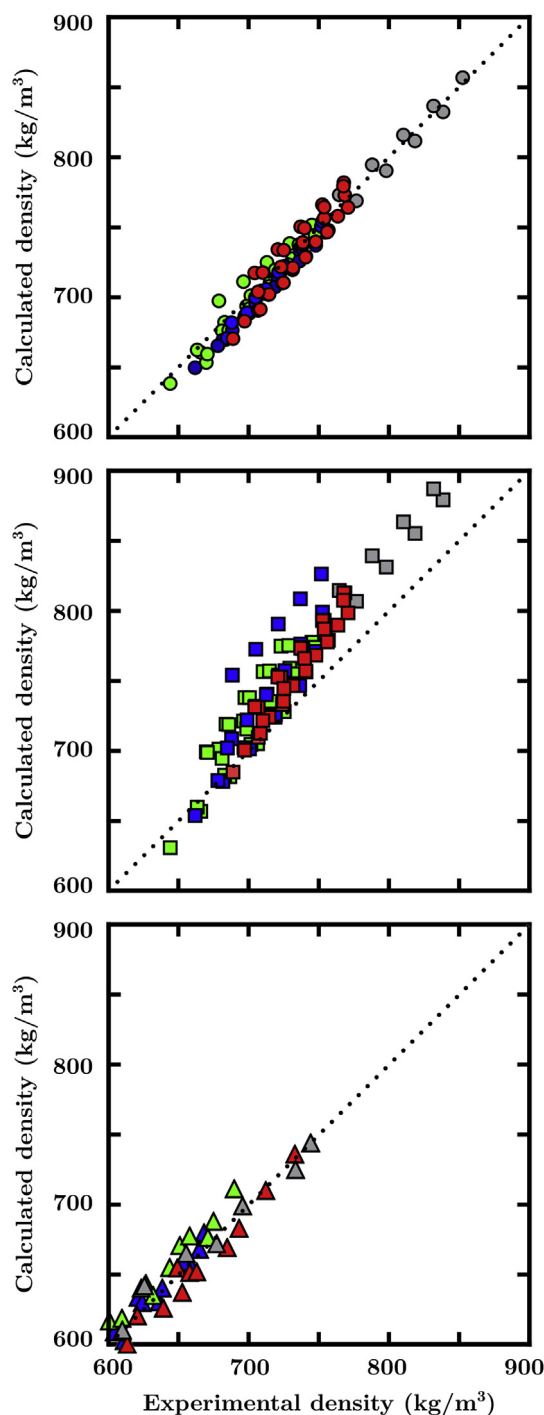


Fig. 2. Comparison of experimental data and the calculated densities of TraPPE-EH (circles, $R^2 = 0.95$), OPLS-AA (squares, $R^2 = 0.61$) and AUA [14–16] (triangles, $R^2 = 0.96$) for the simulated amines at different temperatures for primary (red), secondary (blue), tertiary (green) amines and diamines (gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$\eta = a + \frac{b}{T} + cT + dT^2 \quad (4)$$

Where a , b , c and d are the correlation parameters. Interpolations of the correlated data were used to compare the simulations to experimental data at the same temperature. It is important to consider that the fit of several experimental samples

has an associated AAD that for our case corresponds to 3.6%.

Although the viscosity is commonly used as a measurement of the resistance of the gliding of molecules, for this work we propose to use the fluidity, defined as the reciprocal value of the viscosity. Fluid viscosity changes rapidly with temperature, therefore small computation differences at low temperatures yield a larger error than the differences at high relative temperatures. On the other hand, for associating fluids such as amines, fluidity follows a smooth curve with temperature [38].

A comparison between the simulated and experimental fluidities for all the studied molecules is shown in Fig. 3. Deviations of bifunctional (BU-DI and PE-DI) and asymmetrical (ME-ET, DM-ET, and ME-DE) amines are excluded from this analysis due to the lack of experimental data. The results for 12 amine molecules (4 primary, 4 secondary and 4 tertiary) previously reported for AUA force-field [14–16] are also shown in Fig. 3. Numerical values of the viscosity as a function of temperature and the experimental data for each of the 19 amines are presented in the Supplementary Material.

Trends reveal TraPPE-EH and AUA can predict accurately fluidities of the studied amines. Whereas, OPLS-AA shows a systematic underprediction. Moreover, unlike to what has been observed for other force fields for amines [18,21], OPLS-AA and TraPPE-EH show no increase in the AAD with increasing molecule size. This same behavior independent of the molecule size was also observed for AUA [14,15].

Absolute average deviations of fluidities for all the studied amines were approximately 28% for OPLS-AA and 12% for TraPPE-EH. For primary amines, deviations of 32% for OPLS-AA and 16% for TraPPE-EH were observed; for secondary amines 24% for OPLS-AA and 9% for TraPPE-EH; and for tertiary amines 26% for OPLS-AA and 10% for TraPPE-EH. Given the greater availability of experimental data for primary amines than for the other amines, deviations are larger for this set.

The deviations observed might be related to the force fields parametrization strategy. In this regard both TraPPE-EH and OPLS-AA have some similarities. For instance, both force fields have in common the torsional potentials and partial charges. However, some differences are also found. First, while OPLS-AA was only parameterized from data at a single temperature, TraPPE-EH involves attempts to fit the density at three temperatures (low reduced temperatures, normal boiling point, and critical temperature). Second, while in OPLS-AA molecules are fully flexibles in TraPPE-EH all bonds are considered rigid. Viscosity coefficients are intimately related to the NMR relaxation times and given that viscosity is in part related to the molecule flexibility, it might cause that the more rigid the molecule the better viscosity predictions [39]. Third, the transferability of the alkane force field must be considered in both cases, more specifically to the methyl and methylene groups. It has been shown, for the united atom versions of OPLS and TraPPE, that viscosity coefficients of alkanes are underestimated over 30% with respect to experimental data [40,41]. Therefore, deviations in amine viscosities, which depend on those parameters, are also expected. Deviations in liquid densities have been also reported by Chen et al. [42] for the OPLS-AA for alkanes. They suggested that the development of independent LJ parameters for the carbon atoms in methyl and methylene groups might improve the results. Following a similar idea for the amines, if better OPLS-AA predictions are required new parameters for every amine group (NH_2 , NH , N) should be considered, since they are currently the same.

OPLS-AA trends in Fig. 3 reveal a displacement in the abscissa, which could indicate a deviation not in the fluidity prediction but in the actual fluid temperature. This is consistent with the differences reported in the phase equilibria of OPLS-AA for amines, where the experimental data are shifted [13]. In liquids, molecules collide

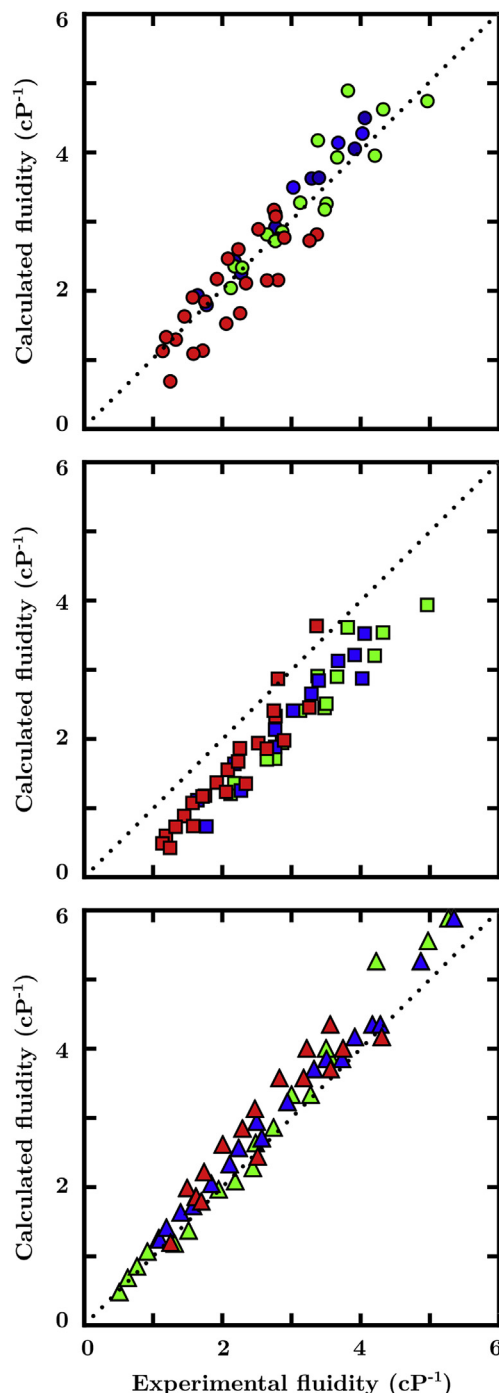


Fig. 3. Comparison of experimental data and the calculated fluidities of TraPPE-EH (circles, $R^2=0.87$), OPLS-AA (squares, $R^2=0.37$) and AUA [14–16] (triangles $R^2=0.93$) for the simulated amines at different temperatures for primary (red), secondary (blue) and tertiary (green) amines. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

frequently with more slowly moving molecules causing a loss in motion, and therefore a resistance to the flow [38]. Increasing the density either by lowering the temperature or increasing the external pressure will increase this effect, thus decreasing the fluidity. Therefore, if the density is overpredicted the fluidity will be underpredicted.

The fraction of free volume is an important characteristic of liquids [43,44], thus, small deviations in the liquid density can lead

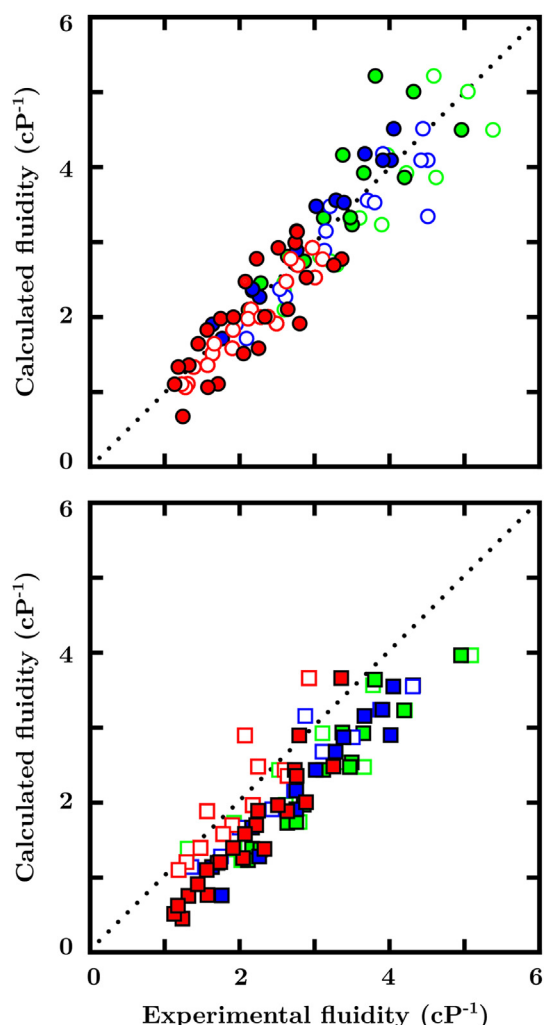


Fig. 4. Comparison of experimental data to: fluidities (filled symbols), and corrected fluidities using T^* (open symbols) for TraPPE-EH (circles, $R^2 = 0.90$) and OPLS-AA (squares, $R^2 = 0.48$). For primary (red), secondary (blue) and tertiary (green) amines. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

to large deviations in the prediction of transport properties. Simulation temperatures were corrected to accurately predict experimental densities. That is, the simulated temperatures were not taken as the actual temperature values and an adjusted temperature (T^*) was used instead. T^* was taken as the value of the experimental temperature that matched the density predicted by the simulations. This is proposed to adjust the simulated data by correcting the simulation temperature to the proper experimental density. Fig. 4 shows a comparison of the experimental and calculated fluidities implementing the T^* correction. The calculated

values for each of the simulated molecules as a function of T^* is presented in the Supplementary Material.

It is seen in Fig. 4 how the temperature correction improves the fluidity predictions (open symbols). As shown in Table 1 deviations decrease once the temperature correction is included. This indicates that the simulation temperature requires a correction in order to obtain a more accurate prediction of fluidities.

This method could be used to correct the simulation temperatures to the actual temperatures by comparing and adjusting to the experimental densities, given that the availability of experimental correlations for the density of different fluids is much higher than the availability of data for transport properties such as viscosity.

However, in cases where there are no available experimental correlations and also for self-consistency of the simulations, it is suggested that the force field parameterization includes viscosity coefficients for the training set of molecules.

4. Conclusions

Molecular dynamics simulations were used to calculate the densities and viscosities of 19 primary, secondary and tertiary amines and they were compared to experimental data available in the literature. The predictive capabilities of two different force fields, TraPPE-EH and OPLS-AA, were assessed for amines and thermodynamic conditions different to the ones used in their training sets. The models were able to accurately predict the liquid density of the molecules and qualitatively predict the behavior of the fluidity. The results revealed that, at low relative temperatures, the accuracy in the prediction of liquid density is critical for obtaining accurate values of the fluidity.

The fluidity is presented as a more convenient property than the viscosity for the evaluation and comparison of force fields at different temperatures. The fluidity follows a smooth curve with temperature, and thus is less subject to give different errors depending on the temperature evaluated.

TraPPE-EH presented the best reproduction of the liquid densities and fluidities for the 19 amine molecules, with an AAD of 1.3% and 12.2%, respectively. In general both properties were well predicted for all the molecules even for those outside the initial parametrization of the force field. OPLS-AA had a much larger disagreement for fluidity 28.1%, which might be related to the deviations found for the liquid densities, AAD of 3.6%.

Moreover, a systematic underprediction of fluidities was observed for OPLS-AA. The quantitative disagreement with experimental results might be caused by mispredictions of the saturation temperature of the molecules. This misprediction was corrected by proposing a new method to evaluate simulations of shear viscosities, the temperature of the simulations was corrected by using a temperature*, which is the value of the experimental temperature that matches the density predicted by the simulations. Given that the availability of experimental data or correlations for temperature are more widely available than viscosity or fluidity data, this method could be used to improve the

Table 1
Absolute average deviations of the force fields with and without correction of temperature.

	TraPPE-EH			OPLS-AA		
	Density (%)	Fluidity (%)	Fluidity corrected (%)	Density (%)	Fluidity (%)	Fluidity corrected (%)
Primary amines	1.4	16.0	8.7	3.1	31.6	15.0
Secondary amines	1.2	9.4	6.6	4.2	24.4	16.2
Tertiary amines	1.2	10.3	7.4	3.2	25.5	23.3
Overall	1.3	12.2	8.4	3.6	28.1	17.6

results obtained by molecular dynamics simulations with different force fields.

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Appendix A. Supplementary data

Force field parameters, simulation results for density and viscosity of each amine with OPLS-AA and TraPPE-EH, experimental viscosities and the regressions used to calculate experimental data is available in the Supplementary Material.

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.fluid.2018.02.021>.

References

- [1] M. Wang, A. Lawal, P. Stephenson, J. Sidders, C. Ramshaw, Post-combustion CO₂ capture with chemical absorption: a state-of-the-art review, *Chem. Eng. Res. Des.* 89 (2011) 1609–1624.
- [2] B. Gurkan, B. Goodrich, E. Mindrup, L. Ficke, M. Massel, S. Seo, T. Senftle, H. Wu, M. Glaser, J. Shah, Molecular design of high capacity, low viscosity, chemically tunable ionic liquids for CO₂ capture, *J. Phys. Chem. Lett.* 1 (2010) 3494–3499.
- [3] P. Lopez-Aranguren, S. Builes, J. Fraile, A. Lopez-Periago, L.F. Vega, C. Domingo, Hybrid aminopolymer-silica materials for efficient CO₂ adsorption, *RSC Adv.* 5 (2015) 104943–104953.
- [4] S. Builes, T. Roussel, C.M. Ghimbeu, J. Parmentier, R. Gadiou, C. Vix-Guterl, L.F. Vega, Microporous carbon adsorbents with high CO₂ capacities for industrial applications, *Phys. Chem. Chem. Phys.* 13 (2011) 16063–16070.
- [5] P. Bernardo, E. Drioli, G. Golemme, Membrane gas separation: a review/state of the art, *Ind. Eng. Chem. Res.* 48 (2009) 4638–4663.
- [6] F. Fazlollahi, S. Saeidi, M.-S. Safdari, M. Sarkari, J.J. Klemes, L.L. Baxter, Effect of operating conditions on cryogenic carbon dioxide removal, *Energy Technol.* 5 (2017) 1588–1598.
- [7] A. Singh, S.I. Olsen, A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels, *Appl. Energy* 88 (2011) 3548–3555.
- [8] G. Puxty, R. Rowland, A. Allport, Q. Yang, M. Bown, R. Burns, M. Maeder, M. Attalla, Carbon dioxide postcombustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines, *Environ. Sci. Technol.* 43 (2009) 6427–6433.
- [9] J. Zhang, P.S. Fennell, J.P.M. Trusler, Density and viscosity of partially carbonated aqueous tertiary alkanolamine solutions at temperatures between (298.15 and 353.15) K, *J. Chem. Eng. Data* 60 (2015) 2392–2399.
- [10] F. Llorell, R.M. Marcos, L.F. Vega, Free-volume theory coupled with soft-SAFT for viscosity calculations: comparison with molecular simulation and experimental data, *J. Phys. Chem. B* 117 (2013) 8159–8171.
- [11] P. Navarro, E.A. Crespo, J. Costa, F. Llorell, J. García, F. Rodríguez, P.J. Carvalho, L.F. Vega, J.A. Coutinho, New experimental data and modeling of glymes: towards the development of a predictive model for Polyethers, *Ind. Eng. Chem. Res.* 56 (2017) 7830–7844.
- [12] R.C. Rizzo, W.L. Jorgensen, OPLS all-atom model for Amines: resolution of the amine hydration problem, *J. Am. Chem. Soc.* 121 (1999) 4827–4836.
- [13] C.D. Wick, J.M. Stubbs, N. Rai, J.I. Siepmann, Transferable potentials for phase equilibria. 7. Primary, secondary, and tertiary amines, nitroalkanes and nitrobenzene, nitriles, amides, pyridine, and pyrimidine, *J. Phys. Chem. B* 109 (2005) 18974–18982.
- [14] G.A. Orozco, C. Nieto-Draghi, A.D. Mackie, V. Lachet, Transferable force field for equilibrium and transport properties in linear, branched, and bifunctional amines I. Primary amines, *J. Phys. Chem. B* 115 (2011) 14617–14625.
- [15] G.A. Orozco, C. Nieto-Draghi, A.D. Mackie, V. Lachet, transferable force field for equilibrium and transport properties in linear and branched monofunctional and multifunctional amines. II. Secondary and tertiary amines, *J. Phys. Chem. B* 116 (2012) 6193–6202.
- [16] G.A. Orozco, C. Nieto-Draghi, A.D. Mackie, V. Lachet, Equilibrium and transport properties of primary, secondary and tertiary amines by molecular simulation, *Oil Gas Sci. Technol.* 69 (2014) 833–849.
- [17] G.A. Orozco, V. Lachet, A.D. Mackie, A molecular simulation study of aqueous solutions of amines and alkanolamines: mixture properties and structural analysis, *Mol. Simulat.* 40 (2014) 123–133.
- [18] F.S. Baskaya, N.H. Gray, Z.N. Gereke, J.R. Elliott, Transferable step potentials for amines, amides, acetates, and ketones, *Fluid Phase Equil.* 236 (2005) 42–52.
- [19] J. Cui, J.R. Elliott Jr., Phase diagrams for a multistep potential model of n-alkanes by discontinuous molecular dynamics and thermodynamic perturbation theory, *J. Chem. Phys.* 116 (2002) 8625–8631.
- [20] S. Patel, C.L. Brooks, CHARMM fluctuating charge force field for proteins: I parameterization and application to bulk organic liquid simulations, *J. Comput. Chem.* 25 (2004) 1–16.
- [21] B.A. Bauer, S. Patel, Condensed-phase properties of n-alkyl-amines from molecular dynamics simulations using charge equilibration force fields, *J. Mol. Liq.* 142 (2008) 32–40.
- [22] S. Turgman-Cohen, E.P. Giannelis, F.A. Escobedo, Transport properties of amine/carbon dioxide reactive mixtures and implications to carbon capture technologies, *ACS Appl. Mater. Interfaces* 7 (2015) 17603–17613.
- [23] X. Yang, R.J. Rees, W. Conway, G. Puxty, Q. Yang, D.A. Winkler, Computational modeling and simulation of CO₂ capture by aqueous amines, *Chem. Rev.* 117 (2017) 9524–9593.
- [24] E.J. Maginn, From discovery to data: what must happen for molecular simulation to become a mainstream chemical engineering tool, *AIChE J.* 55 (2009) 1304–1310.
- [25] C. Coleman, P.J. van Maaren, M. Hong, J.S. Hub, L.T. Costa, D. van der Spoel, Force field benchmark of organic liquids: density, enthalpy of vaporization, heat capacities, surface tension, isothermal compressibility, volumetric expansion coefficient, and dielectric constant, *J. Chem. Theor. Comput.* 8 (2012) 61–74.
- [26] R.A. Zubillaga, A. Labastida, B. Cruz, J.C. Martínez, E. Sánchez, J. Alejandro, Surface tension of organic liquids using the OPLS-AA force field, *J. Chem. Theor. Comput.* 9 (2013) 1611–1615.
- [27] M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, New York, 1987.
- [28] D. van der Spoel, P.J. van Maaren, C. Coleman, GROMACS molecule & liquid database, *Bioinformatics* (2012) 752–753. <http://virtualchemistry.org>. (Accessed 24 January 2018).
- [29] C. Oostenbrink, A. Villa, A.E. Mark, W.F. Van Gunsteren, A biomolecular force field based on the free enthalpy of hydration and solvation: the GROMOS force-field parameter sets 53A5 and 53A6, *J. Comput. Chem.* 25 (2004) 1656–1676.
- [30] W.R.P. Scott, P.H. Hünenberger, I.G. Tironi, A.E. Mark, S.R. Billeter, J. Fennen, A.E. Torda, T. Huber, P. Krüger, W.F. van Gunsteren, The GROMOS biomolecular simulation program package, *J. Phys. Chem. A* 103 (1999) 3596–3607.
- [31] C.L. Yaws, Liquid density of the elements, *Chem. Eng. New York* 114 (2007) 44–46.
- [32] C.F. Spencer, R.P. Danner, Improved equation for prediction of saturated liquid density, *J. Chem. Eng. Data* 17 (1972) 236–241.
- [33] C.L. Yaws, *Thermophysical Properties of Chemicals and Hydrocarbons*, William Andrew Publishing, Norwich, NY, 2009.
- [34] D.S. Viswanath, T.K. Ghosh, D.H.L. Prasad, N.V.K. Dutt, K.Y. Rani, *Viscosity of Liquids: Theory, Estimation, Experiment, and Data*, Springer Netherlands, Dordrecht, The Netherlands, 2007.
- [35] C. Wohlfarth, B. Wohlfahrt, Datasheet from Landolt-Börnstein - Group IV Physical Chemistry Volume 18B: "Pure Organic Liquids" in: M.D. Lechner (Ed.) SpringerMaterials (<https://doi.org/10.1007/b68240>), Springer-Verlag Berlin Heidelberg.
- [36] C. Wohlfarth, Viscosity of Triethylamine: Datasheet from Landolt-Börnstein - Group IV Physical Chemistry Volume 25: "Supplement to IV/18", in: M.D. Lechner (Ed.) SpringerMaterials (<https://doi.org/10.1007/978-3-540-75486-2>), Springer-Verlag Berlin Heidelberg.
- [37] C.L. Yaws, Chapter 3-viscosity of liquid - organic compounds, in: *Transport Properties of Chemicals and Hydrocarbons*, second ed., Gulf Publishing Company, Oxford, 2014, pp. 131–254.
- [38] E.C. Bingham, Viscosity and fluidity - A summary of results. II, *Phys. Rev.* 1 (1913) 96–123.
- [39] J.-P. Korb, N. Voropalawut, B. Nicot, R.G. Bryant, Relation and correlation between NMR relaxation times, diffusion coefficients, and viscosity of heavy crude oils, *J. Phys. Chem. C* 119 (2015) 24439–24446.
- [40] C. Nieto-Draghi, P. Ungerer, B. Rousseau, Optimization of the anisotropic united atoms intermolecular potential for n-alkanes: improvement of transport properties, *J. Chem. Phys.* 125 (2006) 044517.
- [41] D.K. Dysthe, A.H. Fuchs, B. Rousseau, Fluid transport properties by equilibrium molecular dynamics. III. Evaluation of united atom interaction potential models for pure alkanes, *J. Chem. Phys.* 112 (2000) 7581–7590.
- [42] B. Chen, M.G. Martin, J.I. Siepmann, Thermodynamic properties of the williams, OPLS-AA, and MMFF94 all-atom force fields for normal alkanes, *J. Phys. Chem. B* 102 (1998) 2578–2586.
- [43] A. Miller, Free volume and the viscosity of liquid water, *J. Chem. Phys.* 38 (1963) 1568–1571.
- [44] A. Allal, C. Boned, A. Baylaucq, Free-volume viscosity model for fluids in the dense and gaseous states, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* 64 (2001) 011203.