

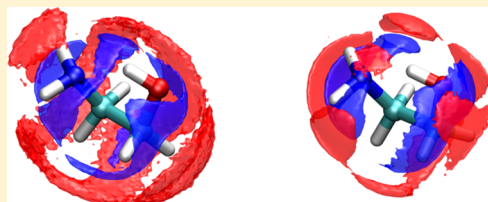
Interactions of Alkanolamines with Water: Excess Enthalpies and Hydrogen Bonding

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S Supporting Information

ABSTRACT: We report a transferable force field to describe the interactions of alkanolamines based on the N–C–C–O backbone with water, derived from a comparison with experimental excess enthalpies. This force field is tested on 2-aminoethan-1-ol (MEA), 2-amino-2-methylpropan-1-ol, 2-amino-butan-1-ol (ABU), and 1-aminopropan-2-ol. These alkanolamines are derivatives of MEA obtained by substitution with methyl and ethyl groups on the carbon atoms of the N–C–C–O backbone. A specific cross interaction site corresponding to the hydrogen bond between the hydroxyl group of the alkanolamine and the oxygen atom of water was introduced in order to reproduce quantitatively experimental excess enthalpies. The transferability of this specific site was assessed by predictions on alkanolamines that were not included in the parametrization data set. New data on enthalpy of mixing for ABU with water are reported, since they were not available in the literature. From the molecular simulations, several microscopic quantities of the alkanolamine–water mixtures were analyzed in order to improve our understanding of these systems. The structure of the solvation shells at varying compositions, statistics of hydrogen bonds, conformations, and energy decompositions served as bases for an interpretation of the molecular reasons underlying the behavior of the excess enthalpy. The prominent result is that water–water interactions play a major role in differentiating alkanolamine–water mixtures, which is a manifestation of the hydrophobic effect. Both the structural and energetic effects observed at the molecular level point to phenomena that have strong composition dependence, in particular, the interplay between the intramolecular hydrogen bond in the alkanolamine and the intermolecular hydrogen bonds with water.



INTRODUCTION

One of the main motivations of this work is to understand the nature of the molecular interactions in a series of mixtures of alkanolamines with water, at varying compositions. This knowledge is essential for the development of physically sound thermodynamic models, namely, group contribution methods that are used in engineering and chemical processing calculations. Primary alkanolamines are among the most important absorbents for CO₂ and other acid gases, with applications in processes of natural gas sweetening and postcombustion CO₂ capture. Some of the alkanolamines, namely, monoethanolamine, are used in existing industrial processes, but it is important to develop better absorbents in view of reducing the cost of CO₂ capture. This task requires compromises between selectivity and high CO₂ load on one side and low energetic cost to regenerate the absorbent on the other. The interactions of the alkanolamine with water are an important element in the thermodynamics of the ternary systems composed of acid gas, amine, and water.

In fluids of polar and associating molecules with complex interactions, such as alkanolamines, where both intra- and intermolecular hydrogen bonds can contribute significantly to the fluid properties, it is difficult to attain a good macroscopic representation, if the nature of the molecular interactions and their evolution with thermodynamic state and composition are not understood. By improving our level of knowledge on the structure and interactions, we expect to contribute to the

development of predictive thermodynamic models. Here we use molecular dynamics simulation with atomistic force fields that describes the molecular structures and interactions in the liquid state and use this molecular model to predict the mixing enthalpy of alkanolamine–water systems.

The present work concerns four alkanolamines based on the N–C–C–O backbone, namely, 2-aminoethan-1-ol (MEA), 2-amino-2-methylpropan-1-ol (AMP), 2-aminobutan-1-ol (ABU), and 1-aminopropan-2-ol (MIPA). The alkanolamines considered are derivatives of MEA obtained by substitution with methyl and ethyl groups on the carbon atoms of the N–C–C–O backbone (Figure 1). Excess enthalpies with water are important to test the interaction model developed here. This property corresponds to the difference between the mixing enthalpy of the real mixture and that of an ideal mixture at the same temperature and pressure. Excess enthalpies are available in the literature for three molecules of this family: MEA, AMP, and MIPA. For ABU we have measured the excess enthalpy with water at 303 K (methods and results given in the Supporting Information).

Several authors have published molecular simulation results on {alkanolamine + water} mixtures. Guskaya and Kusalik reported a molecular dynamics study on ethylene glycol, ethylenediamine, and MEA and their mixtures with water. The

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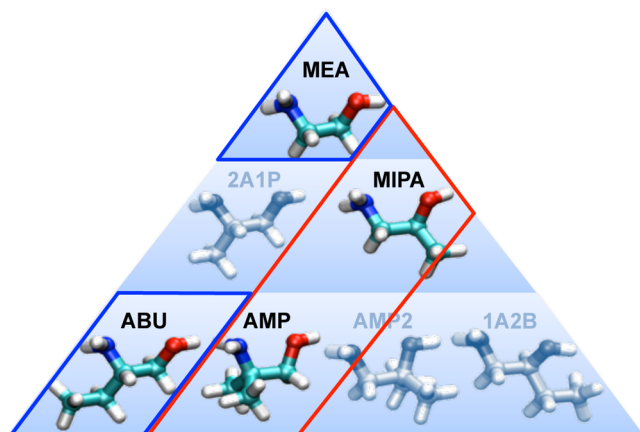


Figure 1. Primary alkanolamines considered in this work, in mixtures with water. Molecules surrounded by blue lines were used to parametrize the force field, through fit to experimental data. The red lines surround the molecules for which predictions of excess enthalpies could be compared to available experimental results. No values of excess enthalpies are reported in the literature for molecules shaded in gray.

microscopic structures of the mixtures (radial distribution functions and composition of solvation shells) were investigated, and energetic quantities were also calculated. However, the authors mention just that there is only qualitative agreement between calculated and experimental heats of mixing. The distributions of conformers of MEA, given by the dihedral angle N–C–C–O, appear to vary widely, between the *gauche* and *trans* conformers, with compositions of {MEA + water}. This probably indicates that statistical sampling was not large enough, mainly due to the small systems sizes,^{1,2} i.e., the number of molecules was too small. The authors identify a tendency of the alkanolamine to adopt *trans* conformations in water-rich compositions, disrupting the intramolecular hydrogen bond in the N–C–C–O backbone.

López-Rendón et al.³ reported a simulation study on pure and aqueous solutions of several ethanolamines. These authors developed a force field model for these alkanolamines and calculated excess volumes for diethanolamine and methyldiethanolamine, in good qualitative agreement with experimental values. Unfortunately, no excess properties are reported for MEA to be compared with our work.

Da Silva et al.⁴ proposed a detailed description of a MEA force field. Since the barriers to internal rotation determine intramolecular hydrogen bonds and the conformation in this molecule, their work emphasized the description of intramolecular potentials. Hydrogen bonding is inferred from analysis of radial distribution functions in pure and aqueous MEA (10 mol %), showing that intramolecular hydrogen bonds of type O–H...N are predominant.

Huang et al.⁵ used quantum chemical calculations (DFT) to study MEA–water complexes containing up to four water molecules interacting with the alkanolamine. They showed that intermolecular hydrogen bonds with water play an important role in the conformations of MEA, leading to a disruption of the intramolecular O–H...N hydrogen bond. The *gauche* conformation remains the majority, even in the presence of water molecules. This had been already established by a conformational study using NMR.⁶

None of the aforementioned studies reported direct comparison between calculated and experimental excess

enthalpies. Dai et al.² published a systematic simulation study on binary mixtures of polar and nonpolar compounds, including the mixture {ethanol + diethylamine}, for which qualitative agreement is obtained with experimental excess enthalpies. These authors analyzed the effect of system size and simulation length on statistical uncertainties. The number of molecules and simulation length of this work reflect the main conclusions of these authors.

Recently Orozco et al.⁷ reported an anisotropic united atom force field for primary, secondary, and tertiary alkanolamines. These authors adjusted parameters of their model to pure-fluid thermodynamic properties and then calculated excess enthalpies with water. The results of excess enthalpy show qualitative agreement with experimental values. In the case of {MEA + water}, excess enthalpy at the minimum is overestimated by about 30% (too exothermic). The trends in excess enthalpy for different alkanolamines obtained from simulation do not correspond to those observed experimentally. This force field model is qualified as transferable by the authors because the intramolecular terms and Lennard-Jones parameters could largely be taken from the previous work of the authors on amines and alcohols. However, it is not clear how the electrostatic charge distributions proposed for this force field were obtained or how one could devise such parameters for new alkanolamines in a compatible way.

From this brief review of the literature, it appears that the mixtures of alkanolamines with water were not studied in detail regarding the microscopic structure and energetic quantities. Furthermore, a truly transferable model, able to represent the conformations and interactions in the mixtures, has not yet been proposed. In the present work, the properties of mixing of four alkanolamines with water were studied using our previously published model for the alkanolamines⁸ and the TIP4P model for water.⁹ Our aim is to investigate if it is possible to predict mixing properties, particularly excess enthalpies, using parameters from the pure compounds with simple combining rules for the unlike interactions or else if particular unlike-interaction parameters are required to represent the properties of the mixtures.

■ FORCE FIELD MODEL AND MOLECULAR SIMULATIONS

The force field for primary alkanolamines with the N–C–C–O “backbone” was developed by our group and reported in a previous publication.⁸ Parameters of this model are compatible with the OPLS-AA force field.¹⁰ However, all the parameters for monofunctional molecules (amine or alcohol) are not transferable to polyfunctional molecules (alkanolamines). This is due to the strong interaction between the –OH and –NH₂ groups when present in the same molecule. Then, our model has specific parameters calculated for this family of alkanolamines, namely, parameters related to torsion energy (involving the two functional groups) and those describing the electrostatic charge distributions. The latter were computed using *ab initio* methods and corrected for polarization effects by a second calculation in the presence of solvating water molecules. Our parametrization of the pure alkanolamine force field does not consist of a single set of partial charges for all the molecules but follows a single (transferable) procedure to determine those charges. It allows the prediction of thermodynamic properties of the pure compounds. The predictive capability of this force field was tested on eight different alkanolamines.⁸

The present work is focused on alkanolamine–water mixtures; the TIP4P model was used for water.⁹

Molecular simulations of the pure phases and mixtures were performed using the DL_POLY¹¹ molecular dynamics package. Systems were simulated in the NpT -ensemble using Nosé–Hoover thermostat and barostat, in periodic cubic boxes. The number of molecules in the system was chosen to correspond to the desired molar fraction with a total number of sites close to those in 500 alkanolamine molecules. Cross Lennard-Jones parameters between nonbonded sites were obtained using a geometrical mean for both site diameters (σ) and well-depths (ϵ). In the same molecule, interactions between particles distant by three or more covalent bonds were also described by Lennard-Jones and partial charges. Interactions of particles separated by exactly three bonds (one to four interactions) were scaled by a factor of $1/2$, as is usual in the OPLS-AA force field.

Intermolecular interactions were computed explicitly up to a cutoff off 12 Å and long-range corrections were applied. The Ewald summation method, parametrized to calculate energies with a relative error below 10^{-3} , which corresponds to a number of five wave vectors in each coordinate of reciprocal space, was used to handle long-range electrostatic interactions. Since in the present study all species are charge-neutral (and not ionic), the effect of using a smaller tolerance for the electrostatic energies is expected to be negligible. In fact, after running some trajectories with a lower tolerance level of 10^{-4} , we concluded that the error in the electrostatic energies is on the order of the statistical uncertainty of the simulations.

Simulation of mixed and pure systems were performed at 1 bar and temperatures close to 298 K, corresponding to experimental temperatures of excess enthalpies available in the literature.^{12–14} Acquisition was done on runs of 2.5 ns after equilibrations of 400 ps, using a time step of 2 fs. Covalent bonds involving H atoms were constrained using the SHAKE algorithm.

Excess molar enthalpies correspond to the difference between the real and the ideal mixing processes and are calculated from simulations of binary mixtures and pure compounds. For each system and composition, enthalpies were calculated from the configurational energy (U^{cfg}), kinetic energy (K), pressure (p), and volume (V):

$$H = U^{\text{cfg}} + K + pV \quad (1)$$

For isothermal mixing, contribution of kinetic energy to excess enthalpies is considered null. It follows that the excess molar enthalpy can be calculated using eq 2, with pure-substance quantities referenced by an asterisk:

$$H^{\text{E}} = U^{\text{cfg}} - \sum_i x_i U_i^{\text{cfg}*} + pV^{\text{E}} \quad (2)$$

In the present systems, excess molar volumes do not exceed a few cubic centimeters per mole. At a pressure of 0.1 MPa, the pV^{E} term is below 1 J mol^{-1} and is therefore negligible. As such, we calculate the excess molar enthalpy from configurational energies according to eq 3:

$$H^{\text{E}} = U^{\text{cfg}} - \sum_i x_i U_i^{\text{cfg}*} \quad (3)$$

The uncertainties in the mixing quantities were evaluated through fits using Redlich–Kister polynomials to points calculated along the composition range from pure water to

pure alkanolamine. In this manner, both the reproducibility of different simulation runs (starting from different initial configurations or using different number of molecules) and the statistical uncertainties intrinsic to the fluctuating quantities during the runs are taken into account in the form of an overall uncertainty (generally $\pm 30 \text{ J mol}^{-1}$).

FORCE FIELD PARAMETRIZATION FOR {ALKANOLAMINE + WATER} MIXTURES

The specific force field previously developed for alkanolamines⁸ using geometric combining rules for the cross-interactions was used to predict mixing properties with water. Figure 2 shows

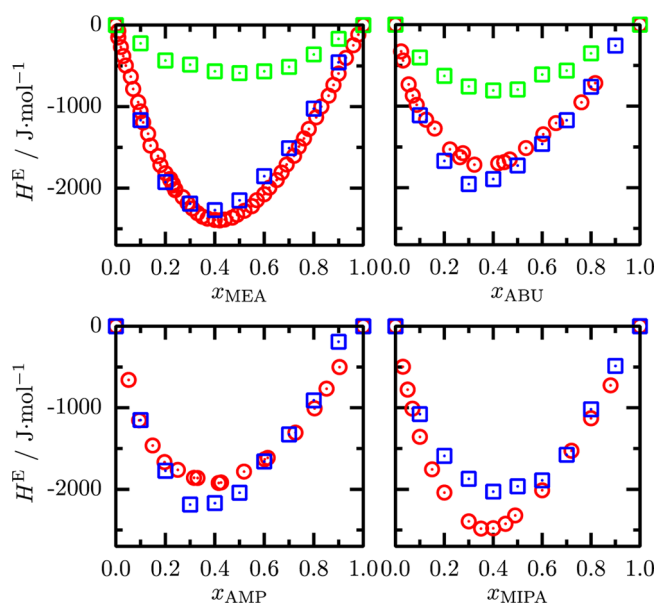


Figure 2. Top row: predicted excess enthalpies (green squares) of {MEA + water} at 298 K (left) and of {ABU + water} at 303 K (right) obtained from pure-fluid parameters only; correlated excess enthalpies (blue squares) of {MEA + water} at 298 K (left) and of {ABU + water} at 303 K (right), obtained with the parametrized force field; experimental values (red circles) of {MEA + water} at 298 K (left) and of {ABU + water} at 303 K (right), obtained from Touhara et al.¹² and in this work, respectively. Bottom row: predicted excess enthalpies (blue squares) of {AMP + water} at 298 K (left) and of {MIPA + water} at 298 K (right), obtained with the new force field, compared to experimental values (red circles) obtained from Mathonat et al.¹³ and Mundhwa et al.,¹⁴ respectively.

the excess enthalpy predicted for aqueous systems of the alkanolamines MEA and ABU at 298 and 303 K, respectively, compared with experimental data. The excess enthalpy is qualitatively well predicted, with a negative value and a minimum at the correct composition. However, the absolute values of the excess enthalpies for MEA and ABU with water are both underestimated. Differentiation observed by simulation is weaker than the one observed experimentally, and in addition, the trend is reversed. This demonstrates that interactions in the mixtures are not well reproduced by the force field using simple combining rules, even if the models for water⁹ and for alkanolamines⁸ render correct energetic and volumetric properties of the pure fluids. The differences observed between simulated and experimental properties are due to interactions between water and alkanolamine molecules, which are not well described by the combining rules.

In these mixtures hydrogen bonding is expected to play a major role in the overall interactions. Regarding the specific structure of the alkanolamines, hydrogen bonds between these molecules and water may not be similar to those observed in the pure fluids. We therefore decided to improve the force field by modifying the interaction between amine and water, in a way that would not change the pure-fluid interactions. We focused on hydrogen bonds to find a way to describe the excess enthalpy. Note that, in the OPLS-AA force field, H atoms in TIP4P water and in the hydroxyl and amine groups are represented by simple point charges, embedded in the Lennard-Jones sites of the O or N atom, respectively. Therefore, molecular association that can be considered as H-bonds depends on a small number of parameters: essentially the charge on the H and on the heavy atom and the Lennard-Jones parameters of the latter. We tried to modify the alkanolamine–water H-bonds by introducing Lennard-Jones parameters to the H-sites involved. We chose not to modify the global combining rules for unlike interactions, because the molecules we consider contain several kinds of functional groups, hydroxyl, amino, and alkyl, which have been optimized for different families of organic molecules within the OPLS-AA framework. We saw no reason to modify the cross-interaction of all of the atomic sites between the alkanolamines and water, which could have uncontrolled consequences for molecules with different substituents or longer alkyl chains. As such, we attempted to identify the minimal number of sites and parameters to modify that lead to the best results for the different {alkanolamines + water} mixtures.

Four possibilities were investigated: (i) adding a site on the hydrogens of the amine group interacting only with the oxygen of water, (ii) adding a site on the hydrogen of the hydroxyl group interacting only with the oxygen of water, (iii) adding a site on the hydrogens of water interacting only with the oxygen of the alkanolamines, and (iv) adding a site on the hydrogens of water interacting only with the nitrogen of the alkanolamines. For each possibility, we attempted to optimize the value of Lennard-Jones parameters (σ and ϵ) so as to reproduce the experimental excess enthalpies of MEA and ABU with water. Among the four alternatives, only one allowed the simultaneous reproduction of the excess enthalpies of MEA and ABU with water at room temperature. As showed in Figure 3, the new Lennard-Jones site was added on the hydrogen of the hydroxyl group of the alkanolamine. This site interacts only with the oxygen atom of water. Optimized cross-parameters are $\sigma = 1.9$

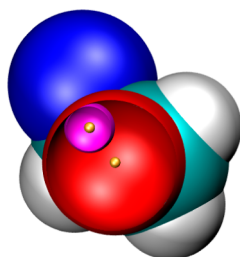


Figure 3. New Lennard-Jones site added for the hydroxyl H of MEA. Yellow dots represent site centers and electrostatic charges. Lennard-Jones sites are represented by the spheres (white for hydrogen, cyan for carbon, dark blue for nitrogen, and red for oxygen). The Lennard-Jones site of the oxygen was sliced to show the two embedded electrostatic charges (oxygen and hydrogen) and the new site on the H (pink) that interacts only with the oxygen of water.

Å and $\epsilon = 6$ kJ mol^{−1}. This value of σ corresponds to a Lennard-Jones sphere embedded inside the diameter of the oxygen site. As such, densities are not modified significantly. Nonetheless, the intensity and directionality of the H-bonds of type O–H...Ow are altered and this is reflected in the excess enthalpy. We remark also that modifying those interactions could have an indirect effect on the intramolecular hydrogen bond of the alkanolamine.

The excess enthalpies of MEA and ABU with water obtained by adding this new site to the force field are shown in Figure 2. The position of the enthalpy minimum is respected for both systems, and calculated values fit correctly experimental enthalpies over the entire composition range. Furthermore, the new cross-interaction leads to a correct differentiation of the two systems.

RESULTS AND DISCUSSION

The quantitative reproduction of the experimental excess enthalpies of MEA and ABU with water means that the cross-interactions are better represented by the force field. The next step is to determine if parameters of the new site are transferable to other alkanolamines in water (not considered in the parametrization step). In Figure 2 the excess enthalpies predicted for AMP and MIPA with water are shown and compared to experimental data. It is seen that the compositions at maximum absolute excess enthalpies are correctly predicted. The values of excess enthalpies are also predicted with a maximum deviation of 0.4 kJ mol^{−1}.

In the Supporting Information (Figure S2), we also compare predicted excess molar volumes for three binary mixtures of alkanolamines and water, namely, MEA, AMP, and MIPA, with experimental data from the literature. Excess volumes were not used at all in parametrizing the force field for the mixtures, and in all three cases, the sign of the excess volume and the position of the absolute maximum are correctly predicted. Agreement is excellent for AMP and MIPA, for which excess volumes are reproduced with errors below 0.2 cm³ mol^{−1}. For MEA, deviations are larger (up to 0.7 cm³ mol^{−1}).

It is interesting to analyze the ability of the present model to differentiate excess enthalpies of aqueous solutions of alkanolamines having close molecular structures (Figure 1): from MEA to AMP, two methyl substituents are connected to the C atom adjacent to the amine group; from MEA to ABU, one ethyl substituent is attached to this carbon. For AMP and ABU, the difference in the interactions with water should be small and will provide a challenging test to the present model.

As seen in Figure 4, the present model for alkanolamine–water interactions does lead to the correct order of the excess enthalpies among the three alkanolamines with closely related structures. Among these calculations, those on AMP are predictions, since the cross-interaction parameters were not derived from data on this alkanolamine.

Once in possession of an interaction model that can represent and predict the energetic properties of mixing, it is interesting to study certain microscopic quantities by simulation to discuss the macroscopic behavior observed experimentally. Structural and energetic information at the molecular level are useful to understand the origin of the excess properties and provide structure–interaction–property relationships. For this purpose the solvation shells will be investigated, statistics of hydrogen bonds will be collected, and the excess enthalpy will be theoretically decomposed into contributions arising from different terms in the interactions.

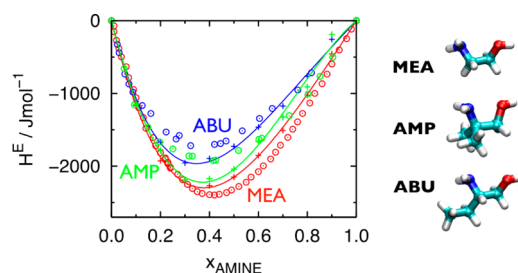


Figure 4. Comparison of excess enthalpies for {ABU + water} (blue), {AMP + water} (green), and {MEA + water} (red). Experimental values, opened circles; calculated values: cross and lines. Experimental and calculated values follow the same order.

Microscopic Structure and Hydrogen Bonds. The differences observed in the solvation shells of MEA and water at different compositions (shown in Figure S3 of the Supporting Information) can be probably explained by changes in the conformations of the alkanolamine dependent on the composition of the mixture, which will be related to intra- and intermolecular hydrogen bonding. Then, one interesting analysis concerns the population of conformers in terms of the O–C–C–N torsion, which lies about 50° from planar (on both sides), as seen in Figure S4 of the Supporting Information. Also, this distribution of dihedral angle is displaced toward larger values upon dilution of the MEA in water, a behavior observed for the other alkanolamines as well. This conformational analysis is consistent with evidence reported by Tubergen et al.,¹⁵ who, using microwave rotational spectroscopy, concluded that the O–C–C–N dihedral angle increases from 57° in the MEA monomer to 75° in the MEA–water complex (see detail in Figure S4).

Other interesting torsional angles in the alkanolamines studied here are H–N–C–C and H–O–C–C, which, together with the O–C–C–N, provide a full description of the relative positions of the amino and hydroxyl groups. A composite plot of the distribution of the three dihedral angles is given in Figure 5. The main result is that with dilution of the amine a new conformer appears, with distinctly new probability zones for $x = 0.1$. This is a very important point, because it shows that the alkanolamine has intra- and intermolecular H-bonds, which vary with compositions. More precisely, for all compositions, conformers with O–H···N intramolecular H-bonds are predominant, whereas with dilution ($x = 0.1$) conformers with N–H···O intramolecular H-bonds are observed. Intramolecular H-bonds refer to O–H···N or N–H···O bonds within the same alkanolamine molecule.

The statistics of the intramolecular H-bonds are plotted in Figure 6, on the basis of the following criteria: one intramolecular H-bond is counted if the distance between H and the acceptor atom X (N or O) is below 2.5 Å and the X–H···Y angle is between 90° and 180° (the angular criterion for these intramolecular H-bonds is more relaxed than is usually taken for intermolecular H-bonds because the proximity of the amino and hydroxyl groups limits their freedom of alignment). It is seen that the intensity of the contour plots for the O–H···N diminishes upon dilution of the amine, whereas the peak for N–H···O increases, albeit at a much smaller intensity. The net result is a reduced number of intramolecular H-bonds of type O–H···N when MEA is diluted in water.

The decrease in the number of intramolecular H-bonds of type O–H···N as the alkanolamines are diluted in water is seen in the different N–C–C–O alkanolamines and is quantified in the plots of Figure 7. The number of such H-bonds decreases in the order ABU > AMP > MEA. With dilution, this number

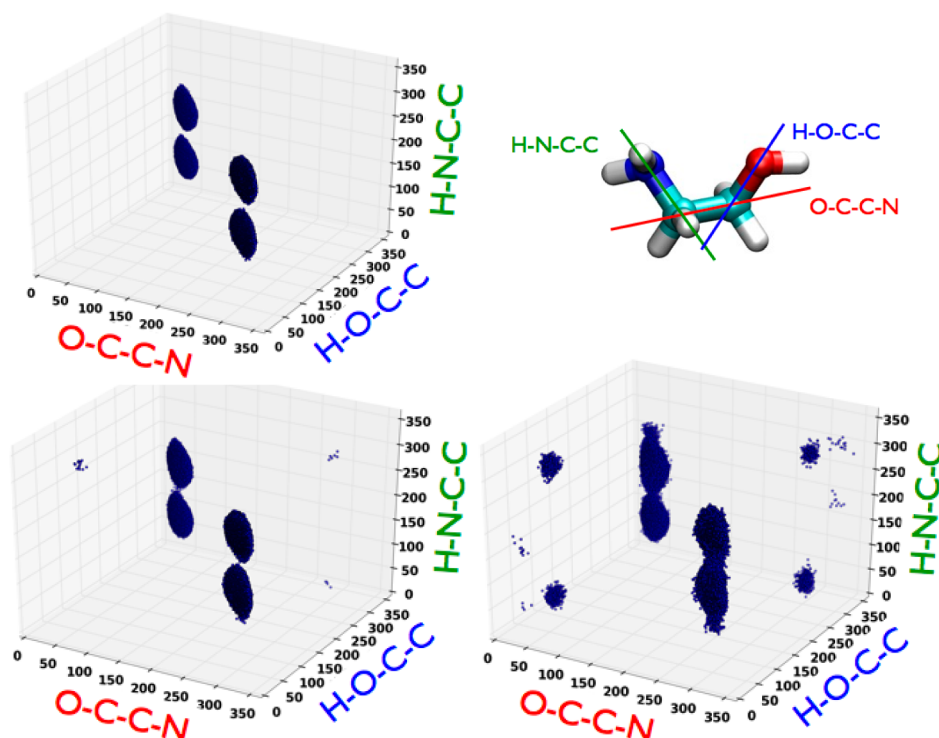


Figure 5. Distribution of the three dihedrals of the MEA as a function of the mole fraction of MEA: $x = 1.0$ (top left), $x = 0.5$ (bottom left), and $x = 0.1$ (bottom right). There are sets of four regions that correspond to equivalent conformations due to symmetry arguments.

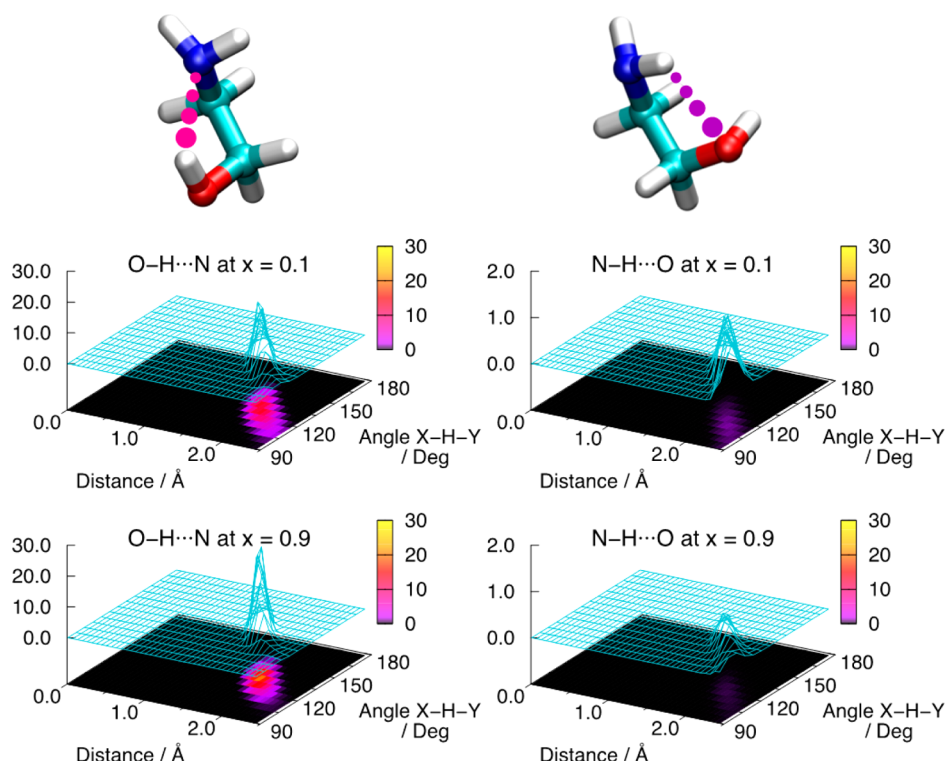


Figure 6. Contour plots of intramolecular H-bonds of MEA as a function of the mixing composition. Images on the left correspond to the conformer with an intramolecular H-bond of type O–H...N and on the right to an intramolecular H-bond of type N–H...O. The two compositions considered are, in mole fraction of alkanolamine, $x = 0.1$ (top figures) and $x = 0.9$ (bottom figures).

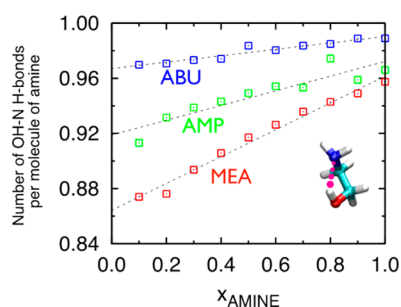


Figure 7. Quantification of the intramolecular H-bonds of type O–H...N for MEA (red), AMP (green), ABU (blue) as a function of the composition of the mixture.

decreases for all alkanolamines. The composition dependence (slopes in Figure 7) is more important for MEA, and the order is MEA > AMP > ABU. As such, the “opening” of the intramolecular H-bond in MEA upon dilution is more pronounced than in AMP and ABU. This is expected to have implications on the excess enthalpy of the {MEA + water} system, through a behavior that should be more distant from ideality than those of {AMP + water} and {ABU + water}, respectively. As expected, the order obtained for the intensity of intramolecular H-bonds disruption with composition is the same as observed for the exothermic effect of excess enthalpies (Figure 4 above). The results on intramolecular H-bonds obtained from the present simulations for MEA are totally consistent with NMR conformational data available in the literature.⁶

Energy Decomposition. Simulation results were used to evaluate the contribution of each kind of binary molecular interactions to the total excess enthalpy. It is possible to

decompose the total excess enthalpy into contributions due to the three different molecule pairs present: alkanolamine–alkanolamine, water–alkanolamine, and water–water. For each pair, the contribution terms of alkanolamines can be compared in order to discuss the relative order of excess enthalpies. Figure 8 shows such comparison between the {MEA + water} and

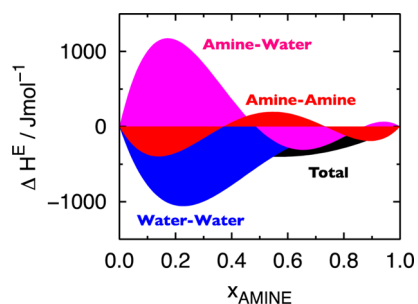


Figure 8. Decomposition of total excess enthalpy into contributions from molecular pairs: alkanolamine–alkanolamine (red), water–alkanolamine (pink), and water–water (blue). Comparison between the {MEA + water} and {ABU + water} mixtures ($\Delta H^E = H^E_{\text{MEA}} - H^E_{\text{ABU}}$).

{ABU + water} mixtures. It is seen that in {MEA + water} the water–alkanolamine contribution is less favorable energetically (positive) than in {ABU + water}. The alkanolamine–alkanolamine contributions are relatively similar between the two systems, whereas the water–water contribution is more favorable in {MEA + water} than in {ABU + water}. This dependence of the excess enthalpy on water–water interactions is a manifestation of the hydrophobic effect: the nonpolar ethyl substituent in ABU causes less favorable water–water

interactions. This happens at compositions where the amine is relatively dilute and behaves as a solute and water as a solvent.

This hydrophobic effect can be seen not only on the energetic decomposition but also in the statistics of intermolecular H-bonds. The criterion now is a H...Y distance below 2.5 Å and a X-H...Y angle between 150° and 180°. In Figure 9, the number of H-bonds in the mixture is compared to

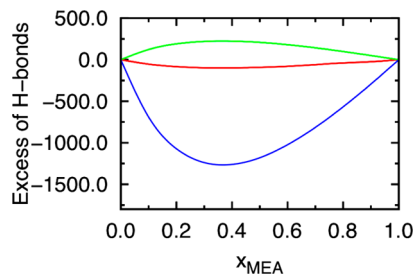


Figure 9. Excess of the statistic of intermolecular H-bonds in mixtures compared to pure compounds for the three main types of H-bonds: Ow-Hw...Ow representing water–water interactions (blue), N-H...O representing alkanolamine–alkanolamine interactions (red), and Ow-Hw...O representing water–alkanolamine interactions (green).

an “ideal” value obtained from a linear fit from numbers of H-bonds at $x = 0$ (pure water) and $x = 1$ (pure amine). To continue the analogy with excess properties, this could be called an “excess of H-bonds” (Figure 9). It is observed that there is a large deficit of Ow-Hw...Ow bonds in the mixture when compared to an “ideal” rule.

CONCLUSION

The main objective of this work was to represent the excess enthalpies of alkanolamines having the molecular backbone N-C-C-O with water, through molecular simulation. The enthalpic experimental data from the literature were completed by measurements of the excess enthalpy of 2-aminobutan-1-ol with water using flow-mixing calorimetry. For the molecular simulations we used a force field model for the alkanolamines developed previously⁸ for the pure compounds and the TIP4P model⁹ for water, with simple combining rules for the cross parameters. This strategy did not provide quantitative predictions of excess enthalpies, even if the exothermic effect and composition behavior were qualitatively reproduced. The results depended only weakly on the structure of the alkanolamine. Therefore, it was not possible to link the molecular structures with the thermodynamic properties. By adding one specific interaction site for the hydrogen bond between the -OH group of the alkanolamine and the Ow atom of water, it was possible to attain a quantitative representation of the excess enthalpies. The parameters of this interaction site were optimized with two alkanolamines in water (MEA, ABU), and then the properties of two other alkanolamines (AMP, MIPA) were correctly predicted.

The methodology to develop force field parameters for both pure alkanolamines and their mixtures with water, as presented in our previous publication⁸ for the pure fluids and here for the mixtures, is transferable to new molecules of the same family. For pure alkanolamines, it is necessary to calculate electrostatic charge distributions and apply a correction taking into account the solvent's polarization effect. In order to represent alkanolamine–water functions, the specific site proposed here

is to be added to describe the O-H...Ow interactions, with transferability of the parameters.

Once in possession of a reliable intermolecular potential model, the microscopic structure of the alkanolamine–water mixtures was studied, namely, the composition of solvation shells, populations of conformers, and hydrogen-bond statistics. The main conclusion of these analyses is that there is a competition between the intramolecular H-bonds of the type O-H...N in the alkanolamines and the H-bonds that these molecules establish with water. The extent to which this intramolecular H-bond is disrupted depends on the alkanolamine and also on the composition of the system. This opening of the intramolecular H-bond could be linked to the deviations from ideal mixing in terms of the excess enthalpy. Following this structural analysis, the energetic properties of the mixtures were assessed by means of decomposition between the different interacting pairs. The prominent result is that water–water interactions play a major role in differentiating {alkanolamine + water} mixtures, which was interpreted as a manifestation of the hydrophobic effect: alkanolamines with larger alkyl substituents led to less favorable interactions among water molecules.

Both the structural and energetic effects observed at the molecular level point to phenomena that have strong composition dependence. This has important consequences toward the development of thermodynamic property prediction models such as, for example, group contribution schemes. The information gathered in the present study from simulation and also spectroscopic data from the literature⁶ can hopefully be used to improve group contribution methods by taking into account local composition effects.

ASSOCIATED CONTENT

Supporting Information

(i) Experimental enthalpies of mixing of 2-aminobutan-1-ol (ABU) with water measured using a flow calorimetry method, (ii) prediction of excess volumes of several alkanolamines with water using the present force field, (iii) spatial distribution functions illustrating the structure of the solvation shells around alkanolamine (MEA) and water in their mixtures, and (iv) histograms with populations of conformers of alkanolamine (MEA) in solution obtained from molecular simulation. This material 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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