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A first-principles based force-field for Li^+ and OH^- in ethanolic solution

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We report on the development of force-field parameters for accurately modeling lithium and hydroxide ions in ethanol in solution. Based on quantum calculations of small molecular clusters mimicking the solvent structure of individual ions as well as the solvated LiOH dimer, significant improvements of off-the-shelf force-fields are obtained. The quality of our model is demonstrated by comparison to *ab initio* molecular dynamics of the bulk solution and to experimental data available for ethanol/water mixtures. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824300>]

I. INTRODUCTION

The most common route to metal oxide nanoparticles is nucleation from solution. This “wet” synthesis approach offers a manifold of advantages including mild reaction conditions and the possibility to control particle shape or even inner structure via the appropriate choice of the solvent and additives to the solution. On the solute side, alkali hydroxides such as LiOH are key players as they are often used as source of hydroxide ions for metal hydroxide precursor and more mature metal oxide nanoparticle formation, while the Li^+ ions remain in solution.^{1,2} The structure and dynamics of alkali hydroxide solutions have been intensely studied for aqueous systems – we refer to the study of Megyes *et al.*³ on aqueous sodium hydroxide solution for a nice overview – but there is a vast lack of information for non-aqueous solutions. This is an unsatisfying situation as metal oxide nanoparticles are commonly synthesized from ethanolic solution.

With the age of rational nanoparticle design at reach, detailed knowledge of the solvent and solute structure is of crucial importance. In this regard, molecular simulations complement experiments and offer insights at a unique level of detail.⁴ A requisite to this are reliable interaction models, force-fields, allowing for the dynamic simulation of model systems comprising thousands to millions of molecules to mimic nucleation from solution, crystal-solvent interfaces, or even dispersed nanoparticle solutions.⁵ While there are well-established force-fields for aqueous solutions, their transfer to alcoholic solution leads to uncontrolled inaccuracies, and as we show here, sometimes even qualitatively wrong results. In what follows, we focus on Li^+ and OH^- ions in ethanolic solution, a widely used agent in nanoparticle syntheses.⁶ In lack of detailed experimental information, *ab initio* calculations of molecular clusters are used to develop the force-field, while benchmarking is performed by Car-Parrinello molecular dynamics (CPMD) simulations of the bulk solution and by comparison to experimental characterization of LiOH solvation in ethanol/water mixtures.

II. COMPUTATIONAL DETAILS

A. *Ab initio* calculations of clusters

As starting points to force-field development, we constructed a series of molecular clusters to mimic the first solvation shell of Li^+ and OH^- ions, and the coordination of the LiOH dimer by ethanol molecules. After structure optimization, the resulting potential energy of formation was compared to identify favorable coordination arrangements. All calculations were performed utilizing the *NWchem* package using the standard Hartree-Fock algorithm.⁷ The basis sets were chosen as cc-pvdz for carbon and alkyl hydrogens and aug-cc-pvdz^{8,9} for lithium, oxygen, and hydroxy hydrogens, respectively. This choice was motivated from recent studies on similar systems.^{3,10} The final structures were subject to single-point energy calculations at the MP2 level of theory. Binding energies were corrected by using the counterpoise method to account for the basis-set superposition error.¹¹

B. Molecular dynamics using force-fields

We tested three different force-fields for LiOH in ethanolic solution and ethanol mixture with water. The first model is the well established OPLS-AA (optimized potential for liquid simulation-all atom) force-field¹² for liquid ethanol, which was successfully used to determine dynamic properties of liquid ethanol¹³ and mixtures with water.¹⁴ In the mixture simulations, water was modeled by the modified TIP3P¹⁵ force-field. Parameters for LiOH in combination with those force-fields are not available and have been parameterized in this work. This model will be referred as FF1-NonPol.

Our second approach is to use a polarizable interaction model for simulating alkali hydroxides in aqueous solution relying on polarizable interaction models as suggested by Dang and Chen (DC97).^{16–19} We combined this force-field for water and LiOH with a polarizable OPLS force-field for ethanol.²⁰ In theory, this force-field should be transferable and hence we used the parameters as-they-are as in the available standard

force-field. Note that we do not apply the multistate empirical valence bond model to account for proton-transfer to keep computational costs reasonable.

The third approach was to adapt a flexible charge model (referred to as FF2-ChEQ) to explicitly allow charge transfer. Here, we use the charge equilibrium method by Rappé and Goddard²¹ in the extended version of Zhang and Fournier.²² In this method, the atomic charges are determined by equalizing the electronegativity of all atoms. The energy as a function of the charge can be obtained using a fourth order Taylor series combined with an empirical screened coulomb potential J_{ij} . The atomic electronegativity χ_i is then obtained as the first derivative with respect to the atomic charge q_i

$$\chi_i = \frac{\partial E}{\partial q_i} = \chi_i^0 + 2\eta_i^0 q_i + \frac{1}{2} \left(\frac{\partial^3 E}{\partial q^3} \right)_0 q_i^2 + \frac{1}{6} \left(\frac{\partial^4 E}{\partial q^4} \right)_0 q_i^3 + \sum_{j \neq i}^N J_{ij} q_j. \quad (1)$$

After charge transfer in the relaxed state, all atomic electronegativities must be equal $\chi_1 = \chi_2 = \dots = \chi_N$ and the overall net charge is preserved $\sum_i^N q_i = q_{net}$. The resulting set of nonlinear equations can be iteratively solved to obtain the best atomic charges. We implemented this method in *LAMMPS* using an extended Lagrangian formalism.²³ The Taylor coefficients are atomic parameters and have been parameterized in this work. This model was applied exclusively for LiOH and pure ethanol.

C. Classical molecular dynamics

We performed most of the classical molecular dynamic simulations utilizing the *LAMMPS* simulation package.²⁴ The only exception are the simulations including induced dipole interactions, for which we used the *TINKER* software package.²⁵ The integration time step is 1 fs and short-range non-bonded interactions are cut off at 0.9 nm. Long-range electrostatic interactions are calculated by the standard Ewald summation with a real space cutoff of 1.2 nm. Three different simulations were set up. The first is a small cubic box containing 63 ethanol molecules and one LiOH dimer. This setup is still accessible to *ab initio* molecular dynamics. Moreover, a second, larger box with 656 molecules and 4 LiOH ion pairs

representing a solution with a concentration of 100 mmol/l was prepared. We have no reliable data for the solubility in pure ethanol, but from extrapolating experimental data, this amount of LiOH should still be soluble. Finally, a third simulation was set up containing 360 ethanol molecules, 640 water molecules, and 22 LiOH ion pairs. This is equivalent to a salt-free ethanol mass fraction of 0.589 and the reported solubility of 1.91 kg LiOH/100 kg solution (≈ 0.68 mol/l).²⁶

In all setups, the temperature was set to 293 K using a Nosé-Hoover thermostat (applied to the movement of atomic centers, only). The volume was averaged by a *NpT*-ensemble simulation (1 ns for the small box and 10 ns for the larger boxes) according to a pressure of 1 atm. After that all simulations followed the protocol of a short equilibration (2 ps small and 50 ps large box) and a production run (150 ps small and 10 ns large box) to gather statistical data.

D. Car-Parrinello molecular dynamics

For our *ab initio* simulations, we used the *CPMD* program.²⁷ As setup we took the small box from the classical MD simulation. Simulation times and molecule numbers are the same. No volume averaging was performed and the cell parameters are from the FF1-NonPol force-field. The timestep was 0.145 fs (6 a.u.) and the fictitious electron mass was 700 m_e . We used the PBE functional²⁸ and Vanderbilt ultra soft pseudo potentials.²⁹

III. MODEL DEVELOPMENT

As starting point to force-field parameterization, we first analyzed the structure of the isolated ion-solvent shell clusters. The lithium cation was preferentially found in the 4-fold tetrahedral coordinated structure (Figure 1(a)). For the hydroxide anion, we also observed a quasi-tetrahedral coordination for the oxygen, in which one ethanol molecule is replaced by the hydrogen atom (Figure 1(b)). The $H_{Hyd}-O_{Hyd}-H_{Et}$ angles of 108.3° are slightly off the perfect tetrahedron with 109.5° . This provides more flexibility to the ethanol molecules and widens the $H_{Et}-O_{Hyd}-H_{Et}$ angle to 111.3° . It should be noted that due to this trend even a second structure with 4 ethanol in a quasi-pyramidal coordination is only 0.7 eV less stable. The structure for the ion pair LiOH is basically a combination of the tetrahedral $[Li(EtOH)_4]^+$

FIG. 1. Hartree-Fock optimized clusters of Li^+ and OH^- coordinated by ethanol. The $Li \cdots O_{Et}$, $O_{Hyd} \cdots O_{Et}$, and $Li \cdots O_{Hyd}$ distances were found as 1.875 Å, 2.683 Å, and 1.775 Å, respectively. (a) $[Li(EtOH)_4]^+$, (b) $[OH(EtOH)_3]^-$, (c) $[LiOH(EtOH)_6]$.

TABLE I. Lennard-Jones parameters for Li^+ and OH^- . Parameters for the hydrogen atoms were only added in case of the FF2-ChEQ model to enhance overall simulation stability.

	DC97	FF1-NonPol	FF2-ChEQ
ϵ_{Li} (eV)	0.0072	0.0017	0.0075
σ_{Li} (Å)	1.51	1.94	1.59
ϵ_{O} (eV)	0.0079	0.0070	0.0033
σ_{O} (Å)	3.52	3.67	2.81
ϵ_{H} (eV)	...	...	0.0020
σ_{H} (Å)	...	...	0.40

and a quasi-pyramidal $[\text{OH}(\text{EtOH})_4]^-$ cluster (Figure 1(c)). Therein, an ethanol molecule is, respectively, replaced by Li^+ or OH^- . From this gas-phase cluster, we created a fitting set of structures by varying the inter-molecular distances and angles. On this basis, we optimized van-der-Waals (vdW)-parameters of Li^+ and OH^- in the nonpolarizable (FF1-NonPol) and the flexible charge model (FF2-ChEQ) with respect to the reference set utilizing the *NLopt* library.³⁰ Keeping the parameters for ethanol and water unchanged taken from OPLS/TIP3P, the optimization comprises two steps: first, a global optimization with a controlled random search and second a local refinement with a simplex algorithm. Assuming a van-der-Waals + Coulomb type interaction model, we optimize Lennard-Jones parameters ϵ and σ for the “heavy” atoms Li and O (Table I)

$$V_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right). \quad (2)$$

For the fixed-charge electrostatic interactions, we used point charges ($q_{\text{Li}} = 1e$, $q_{\text{O}} = -1.2e$, $q_{\text{H}} = 0.2e$). In the case of the flexible charges, we followed the strategy of Oda and Takahashi³¹ to fit the charge equilibrium parameters (Table II) to reproduce restrained electrostatic potential (RESP) charges for our clusters.

For the nonpolarizable force-field, the standard mixing rules fail to describe both the ethanol-ion and the ion-ion interactions simultaneously. This is mainly due to the neglected charge transfer from the ions to the ethanol molecules when using fixed charges. A way to improve is to not rely on mixing rules and assign specific parameters for the Li–O non-bonded interaction and try to diminish the effect of too strong electrostatic interactions. While in principle possible,

TABLE II. Coefficients for the flexible charge model (FF2-ChEQ). The function J_{ij} for the screened coulomb potential is taken from Zhang and Fournier’s version.²²

	χ^0 (eV)	η^0 (eV)	$\left(\frac{\partial^3 E}{\partial q^3} \right)_0$ (eV)	$\left(\frac{\partial^4 E}{\partial q^4} \right)_0$ (eV)
Li	1.39	5.24	2.60	5.06
O _{Hyd}	7.21	2.19	−0.27	22.90
H _{Hyd}	0.51	12.71	−1.25	19.32
C _{Et}	5.07	3.79	−1.73	14.46
O _{Et}	9.58	7.79	3.71	10.41
H _{Et}	4.72	5.63	12.00	−2.82
H(O) _{Et}	4.64	6.73	3.71	6.87

TABLE III. Buckingham parameters for the refitted Li^+ , OH^- , and EtOH.

	Li–O _{Et}	O–O _{Et}	Li–O _{Hyd}
A (eV)	1850.111	5384.290	15.65
ρ (Å ^{−1})	0.2476	0.3041	0.9972
C (eV)	29.053	286.941	−19.109

this leads to non-physical type of parameters, e.g., attractive R12 and repulsive R6 contributions. This correction is only short-ranged, but for long-range interaction the effect should not be too dramatic since the net charge of the whole cluster is conserved anyway. A second problem with the simple Lennard-Jones type of potentials is the generally too steep R12 repulsion. Particular for the ion-ion interactions it is not possible to find proper parameters. For that reason, we changed the function type for the dominant interactions of lithium–oxygen and oxygen–oxygen to a Buckingham potential

$$V_{\text{Buck}}(r) = A \exp(-r/\rho) - \frac{C}{r^6}. \quad (3)$$

This potential allows a softer, exponential repulsion. It should be mentioned that this improvement of accuracy comes at loss of transferability via the Lorentz-Berthelot combining rules. The resulting parameters are given in Table III. Note that the $\text{Li}^+ \cdots \text{OH}^-$ van-der-Waals interactions are modeled completely repulsive (C is negative) to compensate the effect of the missing charge transfer.

In the case of the flexible charge model, the gas-phase binding energies are poorly reproduced. In general, charge equilibrium methods are not able to represent long-range gas phase interactions and dissociations as no distance dependence of charge transfer is accounted for. Focusing on the contact ion pair, here we only adjusted the Lennard-Jones parameters of the repulsive close-range part of the binding energies based on the cluster calculations. Note that we also added individual parameter sets for the non-aliphatic hydrogen atoms to improve the numerical stability of our simulations. All binding energies for the dominant interactions are shown in Figure 2.

IV. BENCHMARKS

A. LiOH–ethanol structure

This can be rationalized by considering no, 1, or 2 chains of hydroxy groups from ethanol molecules $[\text{Li}(\text{EtOH})_n\text{OH}]$ between the lithium and hydroxide ions. Here, no hydroxy groups imply a contact ion pair (Figure 3(a)), which basically would hint at precipitation. In this case, obviously the coordination number of ethanol molecules decreases because the ions now are coordinated to each other. When having one bridging OH group, the ions are less close and fully coordinated by shared ethanol molecules. Two groups mean no shared ethanol molecules in the coordination sphere, see Figure 3(b).

As reference to the solvation of separate Li^+ and OH^- ions versus the LiOH contact ion pair, we rely on CPMD

FIG. 2. Binding energies and distance dependence of dominant interactions in small Li^+ , OH^- –ethanol clusters. Note that the flexible charge model implies charge transfer over any distance, including in principle separated atoms, and is thus unable to account for absolute binding energies.

calculations. Even though the simulated time frame is rather short, we observed discriminable local solvate structures (radial distribution function is shown in Figure 4). Like in the gas-phase calculations, the coordination of Li^+ and OH^- ions in solution are mainly tetrahedral $[\text{Li}(\text{EtOH})_4]^+$ and quasi-tetrahedral $[\text{OH}(\text{EtOH})_3]^-$ (coordination numbers are shown in Figure 5). They are not in a direct contact and form the 2-bridge structure, that is, there are no shared coordinating ethanol molecules. We observe a frequent exchange of coordinating ethanol molecules but never a closer contact than two bridging hydroxy groups. After several picoseconds, the ions separate even more into the 3-bridge conformation.

FIG. 3. Solvated ion pair structures as obtained from MD simulations. Li^+ and OH^- are shown as spheres. The corresponding $\text{Li} \cdots \text{O}_{\text{H}_{\text{yd}}}$ distance was found as 1.9 Å and 4.6 Å for the (a) contact and (b) bridged ion pair, respectively.

FIG. 4. Radial distribution function $g(r)$ and number of particles $n(r)$ within distance r for Li and $\text{O}_{\text{H}_{\text{yd}}}$. The unchanged parameters from the DC97/OPLS model yield a contact ion pair (red curve). The new parameters with fixed charges FF1-NonPol, respectively, flexible charges FF2-ChEQ (blue and green) show no contact ion pair, but a more explicit shell structure leading to two peaks in $g(r)$.

FIG. 5. Number of particles $n(r)$ within distance r for Li , $\text{O}_{\text{H}_{\text{yd}}}$, and O_{Et} . The coordination number from the CPMD simulation (black) is used as reference. All force-fields reproduce the 4-fold coordination of Li^+ . However, OH^- is always over-coordinated. Only the flexible charge approach (green) results in an almost similar coordination to that of the reference CPMD simulations.

The force-field simulations are initiated from the same starting point as used in the CPMD simulation. However, for the DC97/OPLS force-field, we immediately observe a metastable 1-bridge conformation which soon collapses into a contact ion pair. This is in line with the large simulations with several ions where almost all LiOH precipitates within few nanoseconds. Simulations with single ions show that the coordination of lithium is also tetrahedral but with shorter Li–O distances. However, the hydroxide, despite the multipole contribution, is found as quasi-octahedral $[\text{OH}(\text{EtOH})_3]^-$ coordinated. The DC97/OPLS model is thus not suitable for mimicking a dispersed LiOH solution.

Our first parameterized force-field FF1-NonPol successfully reproduces the 2-bridge conformation for the ion pair. It also shows the same ion separation into the 3-bridge or next solvation shell. The distances differ by up to 0.4 Å, but the average structure is reproduced fairly well. The $[\text{Li}(\text{EtOH})_4]^+$ cluster is almost perfectly reproduced. Unfortunately, the hydroxide still tends to be over-coordinated and lead to a 3+3 coordination $[\text{OH}(\text{EtOH})_{3+3}]^-$. Though still inaccurate, this solvation structure contains partly the quasi-tetrahedral coordination. Moreover, the unrealistic tendency to contact ion pair formation as observed for the DC97/OPLS model is amended. This is not a feature but allows the cluster to have similar bridging patterns as in the CPMD simulation.

The overcoordination of the hydroxide finally motivated for the flexible charge approach. Indeed, the FF2-ChEQ model simulations show less coordination for the hydroxide. We mostly find a $[\text{OH}(\text{EtOH})_4]^-$ and rarely a $[\text{OH}(\text{EtOH})_3]^-$ conformation. While still not in full agreement with the CPMD simulation, this is an improvement over the conventional force-fields. However, unlike the CPMD results, the ion pair was also observed to temporarily reside in a 1-bridge state. Besides this, it shows the same behavior as the FF1-NonPol force-field.

B. Solution stability

1. Anhydrous LiOH in ethanol

The stability of the solution was investigated using the large box simulation, which are unfortunately too demanding for the CPMD approach. For the DC97/OPLS model, we immediately observe precipitation leading to LiOH agglomerates. The average density of the “solution” was found as 767 kg/m^3 . In contrast to this, for our new fixed-charge FF1-NonPol model, the solution stays stable exhibiting an average density of 771 kg/m^3 . Our flexible charge FF2-ChEQ model has also an improved stability, but still ions occasionally form contact ion pairs (av. density 786 kg/m^3). However, none of them aggregated to a larger particle as in the DC97/OPLS simulations. Nevertheless, the dissociation dynamics are problematic due to the earlier mentioned short-comings of the charge equilibrium method. Indeed, an once formed contact ion pair was never observed to split again. All solutions show a decreased density compared to pure ethanol solution (about 790 kg/m^3).

2. LiOH in ethanol-water

Seeking comparison with experimental data, we face the problem that almost all reported experiments were dedicated to aqueous solution. With respect to ethanolic solution, the closest we found are measurements related to LiOH solubilities in water-ethanol mixtures of various fractions.²⁶ We therefore transferred our model to a ethanol-water mixture at the limit of solubility. As our actual focus is ethanol, as model system we only chose the experimental data point related to the highest ethanol content of 9 EtOH:16 H₂O. For this solvent, the reported density of the saturated salt solution reads 908 kg/m^3 .

In analogy to our molecular simulations related to pure ethanol solvent, the DC97/OPLS model did not show a stable solution and LiOH precipitates quickly to small aggregates. The density of this model system was found as 929 kg/m^3 – which is far from the experimental value as precipitation spoils the salt effect occurring in a dispersed ionic solution. On the other hand, our FF1-NonPol force-field leads to more realistic Li–OH interactions and the solution remains stable. Therein, the ions are dispersed (both Li^+ and OH^- were found to clearly prefer nearest neighbor coordination by water) and account for a salt effect on solution density of 892 kg/m^3 which is quite close to the experimental value. This is a good result, considering that no further adjustments were made for the water interaction potentials and our new model parameters were used straight.

V. CONCLUSION

Our studies show that ion-solvent interaction model parameters for aqueous solution cannot be simply transferred to organic solvents or even their mixtures with water. We therefore derived new parameters based on gas-phase *ab initio* calculations. As benchmarks, the new force-field was confirmed to reproduce most of the structural features as observed from *ab initio* MD simulations. While we lack experimental data of transport and thermodynamic properties such as solution enthalpies, we confirmed the stability and densities of different solutions in good agreement with the experiment. From the different modeling approaches applied, we suggest the fixed-charge nonpolarizable type (FF1-NonPol) as an appealing compromise of accuracy and general transferability to various ethanolic solution scenarios.

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