Ab Initio Molecular Dynamics Approach to a Quantitative Description of Ion Pairing in Water

Eva Pluhařová,[†] Ondrej Marsalek,[†,§] Burkhard Schmidt,[‡] and Pavel Jungwirth*,[†]

[†]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 16610 Prague 6, Czech Republic

[‡]Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, D-14195 Berlin, Germany

ⓈSupporting Information

ABSTRACT: Ion pairing of lithium and fluoride in water is described quantitatively using ab initio molecular dynamics simulations. We design a reliable computational protocol for evaluating the ion–ion potential of mean force using density functional based simulation methods. By comparison to classical molecular dynamics with empirical force fields, we establish the statistical error of the procedure. We also check the accuracy of the electronic structure description by comparison to experimental structural data and to higher-level calculations for model systems. The present approach not only points to deficiencies in force field calculations of potentials of mean force for difficult cases of high charge density ions like the aqueous lithium fluoride pair but also allows extraction of electronic information, such as the amount of charge transfer to solvent and its dependence on the ion–ion distance.

SECTION: Liquids; Chemical and Dynamical Processes in Solution
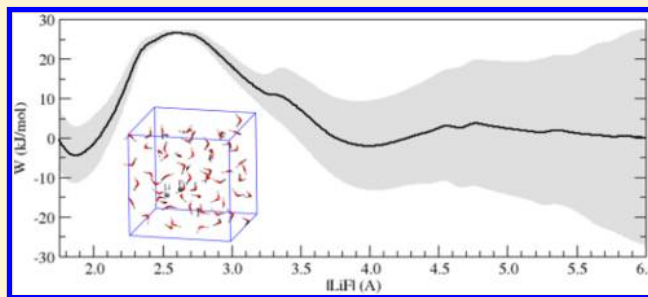
Ion pairing is association of oppositely charged electrolyte ions in solution. Ion pairs are held together primarily by Coulomb attraction (screened by the solvent), without formation of a covalent bond.[1] Bjerrum originally suggested that all pairs of oppositely charged ions closer than a certain distance should be treated as associated ion pairs, whereas those at larger distances should be considered as free.[1,2] Multistage ion pairing, that is, geometries ranging from a contact ion pair (CIP), where the partners are in direct contact, over a solvent-shared ion pair (SIP) with a solvent molecule in-between the ions, to a (double) solvent-separated ion pair (2SIP), where the primary solvation shells of both ions remain essentially intact, was suggested by Eigen and Tamm in order to interpret sound absorption relaxation processes in electrolyte solutions.[1,3] Subsequently, the widely used Pitzer's model of interacting ions was able to provide thermodynamic properties such as activity coefficients without considering ion pairing explicitly.[4,5] Nevertheless, more recent spectroscopic experiments and molecular simulations pointed conclusively to the existence of CIPs, SIPs, and 2SIPs as distinct ion pairing geometries separated from each other and from dissociated ions by free-energy barriers.[1,6,7]

In the past decade, the detailed atomistic structure of aqueous salt solutions has been intensely studied experimentally by neutron scattering,[8−11] X-ray diffraction,[8,9,12,13] and dielectric relaxation,[14] as well as computationally employing classical (i.e., with empirical force fields) molecular dynamics (MD) or Monte Carlo simulations.[7,15−17] Theoretical

predictions were shown to be rather sensitive to the details of the empirical force fields;[10,15,18] hence, there is a clear need for independent information based on quantum chemistry approaches, which could also serve for benchmarking and verification of empirical potentials. As our first case study, we have chosen here to investigate the geometrically simple, but electronically nontrivial lithium fluoride ion pair in water. Superficially, this pair of spherical ions could be viewed as having just a single degree of freedom, the distance between the two ions, although in reality, the mechanism of ion pair formation and dissociation in water is somewhat more complicated, involving solvent coordinates.[19] In terms of interactions, LiF(aq) represents a rather pathological case where empirical force fields cannot be expected to be very accurate due to the high charge density of the ions, leading to sizable solvent polarization and charge transfer to solvent. This, together with low solubility of aqueous lithium fluoride[20] points to appreciable ion–ion interactions, where ab initio molecular dynamics (AIMD),[21] typically based on density functional theory in the generalized gradient approximation, can serve as a unique exploratory tool.

Unlike for classical MD, obtaining the free energy as a function of the ion–ion separation in bulk water by computationally much more demanding AIMD is a highly

nontrivial task. While for the former calculations nanosecond time scales are easily accessible, in the latter case, they still remain prohibitively expensive. As a result, there has been only a couple of attempts to evaluate a free-energy profile between two ions in water using Car−Parrinello-type AIMD trajectories; moreover, both have been too short to provide converged results.[22,23] Our goal is to obtain by employing extensive Born−Oppenheimer AIMD simulations the free-energy profile as a potential of mean force (PMF).[24] To this end, we perform a series of simulations constraining the ion−ion distance, evaluating the mean force ($\overline{F}$) along this coordinate, integrating the obtained force curve, and adding the entropic correction due to the different volumes of the phase space sampled in individual sampling windows. To establish the minimum simulation length for obtaining a free-energy profile with a given statistical error, we employ auxiliary classical MD simulations, which can be run for the same system for much longer times.

The resulting aqueous Li−F average force and the corresponding PMF from 50 ps AIMD trajectories for each of the 38 constrained interionic distances (corresponding to almost 2 ns of total simulation time) are shown in Figure 1 and
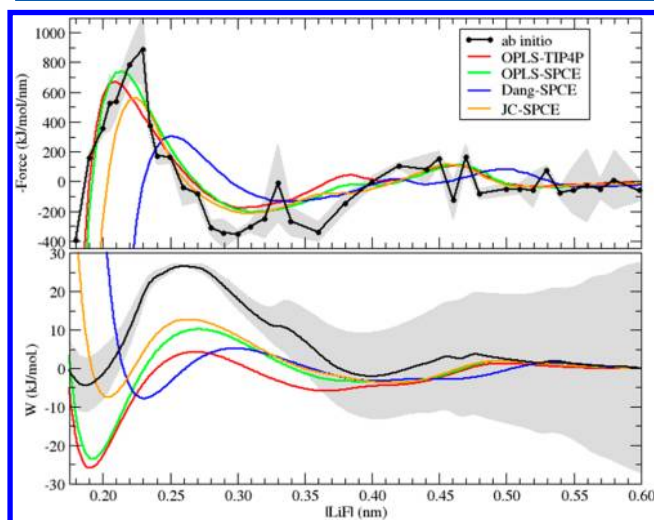

Figure 1. Negative of the mean force (upper part) and integral thereof with entropic correction, that is, the PMF (lower part) along the Li−F coordinate. Ab initio mean forces (black circles) were calculated for 38 points corresponding to 50 ps trajectories after 5 ps of equilibration. The gray area in the upper part indicates the statistical error in force evaluation estimated by the block average analysis method, which being integrated gives an upper bound to the error of the PMF (gray area in the lower part). Comparison is made to 10 ns trajectories per point for the same system simulated using four different empirical force fields (colored lines). All free-energy profiles are normalized to zero at the largest investigated ion−ion separation.

compared to results from classical MD with four different force fields (for further details, see the Supporting Information).[25−29] For AIMD, we also evaluated the mean deviation of the data, displayed in gray around the corresponding curves in Figure 1. While for the mean forces the statistical error is directly obtained from the simulations, for the PMF, we show the accumulated error during the integration procedure. This should be viewed as an upper bound that also somewhat depends on the point where we start the integration. Moreover, for larger interionic separation, the free-energy profile converges to zero (as it should), which indicates that the

actual error is significantly smaller than the estimate that we make here. The CIP, where $\overline{F} = 0$ for the first time upon elongating the Li−F distance, is located at 1.9 Å. The transition state (TS) between the CIP and SIP is located at the Li−F distance of 2.6 Å, lying relatively high, at about 30 kJ/mol, above the CIP. Note that the TS is the point where we chose to start the integration of the mean force. The SIP is then situated at the Li−F distance of 4.0 Å, and its free-energy value is comparable to that of the CIP.

The AIMD PMF can be directly compared to analogous results using empirical force fields (Figure 1). The latter vary substantially, which further justifies using AIMD as benchmark calculations. In general, empirical force fields tend to underestimate the free-energy difference between the SIP and the TS and to overestimate the depth of the CIP. The positions of the two minima vary widely among the empirical force fields, with OPLS providing the least bad qualitative to AIMD. The same force field also best reproduces the free-energy difference between the CIP and the TS but underestimates that between the SIP and the TS. Further, we checked the influence of polarizability, accounted for within classical nonpolarizable MD by effectively rescaling of ionic charges,[30] on the PMF of LiF(aq), but it turned out to be relatively minor in this case (see the Supporting Information).

When constructing free-energy profiles of ion pairing using AIMD, it is crucial to realize that in order to obtain meaningful results, one needs to carefully check two potential major sources of uncertainties. These are the duration of the simulations affecting the statistical error of the result and the level of the electronic structure theory connected with the systematic error. First, we address the issue of the statistical error. The necessary length of the simulation for yielding results with a given statistical error was estimated based on analogous classical MD simulations with an empirical force field, where it is easy to produce relatively long (submicrosecond) trajectories and perform averaging over several blocks of a given length. Figure 2 shows the standard deviation of the mean force as a function of the length of the simulation used in the PMF calculations at a given interionic distance. Four representative
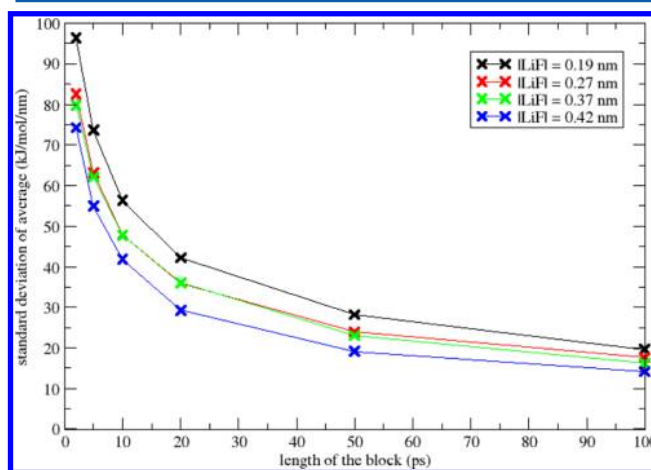
Figure 2. Standard deviation of the mean force acting along the LiF distance for four lithium fluoride separations calculated employing the OPLS/TIP4P empirical force field as a function of the corresponding time span. The 10 ns trajectories were divided into blocks of the respective length, and the average force with the corresponding standard deviation was then evaluated.
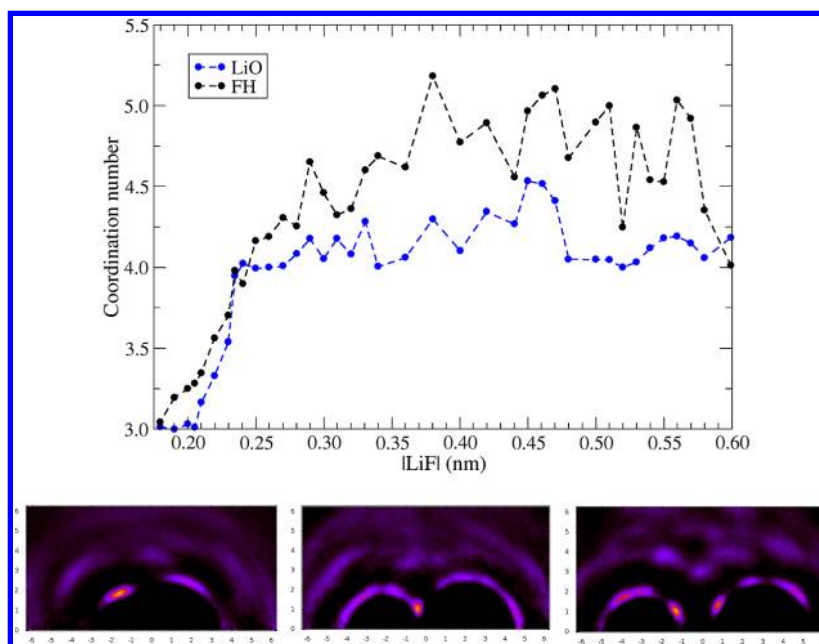
Figure 3. (Top) Number of oxygen atoms in the first solvation shell of Li (blue) and number of hydrogens in the first solvation shell of fluoride (black). Points are connected with a dashed line for guiding the eye. (Bottom) Distributions of oxygen atoms of water molecules around the CIP, SIP, and separated ions geometries of LiF.
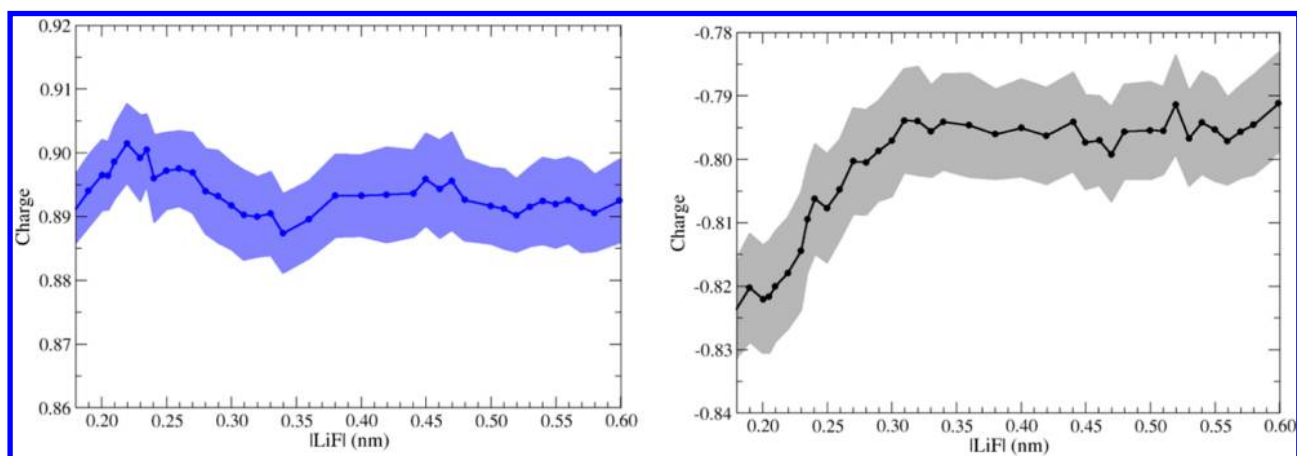
Figure 4. Bader charges (average values with standard deviations) of Li (blue) and F (black) as a function of the LiF separation.

distances were chosen corresponding roughly to CIP, TS, and two points close to SIP. We see that the statistical error is very big for blocks shorter than ∼20 ps, as used in previous studies,[22,23] but drops significantly when extending the block length to about 50 ps, after which it gradually starts to level off. On the basis of this result, we thus chose to collect 50 ps AIMD trajectories for each of the constrained Li−F distances, so that the standard deviation of the mean force could be kept for most points below ∼40 kJ/mol/nm (but occasionally can exceed this value, as, e.g., the point at 3.3 Å in Figure 1).

Next, we focus on potential systematic errors, where exact quantification is more difficult. Single-point energies of several isomers of a model $LiF(H_2O)_{12}$ clusters differing by values of the ion−ion separation and coordination number obtained using the present AIMD setup were compared to results of high-level correlated ab initio methods, yielding a very satisfactory agreement (for details, see the Supporting Information). Another way to validate the employed level of electronic structure theory is comparison of structural

characteristics of the solution to experiment. It has been already shown for individual ions that the current level of density functional theory provides a reliable representation of the local hydration structure of ions as measured by the XAFS spectroscopic technique.[31,32] Radial distribution functions $(g(r))$ of water atoms around ions from our simulations are plotted and discussed in detail in the Supporting Information. The calculated first peak of $g(r_{LiO})$ is situated at 2.05 Å, which is in agreement with previous theoretical studies[33,34] and experiments.[35] The first maximum of $g(r_{FH})$ is located at 1.6 Å, and the first peak of $g(r_{FO})$ is situated at 2.6 Å, which is again in accord with previous ab initio studies.[36,37]

On the basis of the positions of the minima of radial distribution functions, we set the cutoff radius to evaluate the number of oxygen atoms in the first solvation shell of lithium to 2.7 Å and the cutoff radius for the number of hydrogen atoms in the first solvation shell of fluoride to 2.5 Å. The resulting coordination numbers are plotted in Figure 3 as a function of the Li−F distance. The number of oxygen atoms in the first

solvation shell of lithium fluctuates slightly above four for larger Li−F distances but decreases to three at 2.05 Å, where fluoride replaces one of the water molecules. The number of hydrogen atoms forming hydrogen bonds to fluoride fluctuates between 4.5 and 5 for larger Li−F separations and, analogously to lithium, decreases to 3 at around 1.8 Å. Figure 3 also depicts density maps representing distributions of water oxygen around LiF at the geometries of CIP, SIP, and separated ions. While for ions separated by 6 Å the two solvent shells are largely independent of each other, the situation is different at shorter separations. For the SIP, we clearly see the single water molecule shared by the two ions, while for the CIP, this water molecule is replaced by the counterion, which also results in a marked asymmetry of the solvent shell, particularly for the smaller lithium ion.

While the above structural results could be in principle also extracted from classical MD simulations,[7] had we a reliable empirical force field available, in the following, we shall also take advantage of the electronic density provided only by the AIMD simulations. In particular, we use it here to assign for each geometry ionic charges based on the Bader population analysis.[38] Results of this analysis are summarized in Figure 4 as a function of the Li−F distance. The lithium charge is rather constant with Li−F separation, varying between 0.89 and 0.90 |e|, while that of fluoride drops from −0.79 to −0.82 |e| upon formation of the CIP. The distributions of charges along the trajectories are rather narrow for all Li−F separations, with standard deviations of less than 0.01 e, similarly as in previous studies on different ions.[39,40] Hence, we can conclude that there is a non-negligible amount of charge transferred from ions to the solvent. Moreover, the amount of charge transfer is almost constant for lithium, while for fluoride, it slightly decreases with decreasing Li−F separation. We should note here that a partial charge of an ion is not a directly experimentally observable quantity, and thus, it is to some extent definition-dependent. For comparison, we also evaluated partial charges using the natural population analysis (NPA) method (for details, see the Supporting Information). The trends are similar as those for Bader charges, but the absolute values of NPA ionic charges are smaller.

In summary, we have presented here our attempt to obtain a quantitative free-energy profile for an ion pair dissociation in water employing density functional theory combined with a PMF calculation. Lithium fluoride represents a difficult case where empirical force fields tend to fail due to the high charge density of the ions and charge transfer to solvent effects. In contrast, the AIMD description of hydration of the studied ions turns out to be reliable when compared to experiment and, for model systems, to higher-level calculations. Classical MD helps, despite inaccuracies in force fields, to determine the necessary time span of the AIMD trajectories and to estimate statistical errors. In addition to using AIMD to construct the ion−ion PMF, we also took advantage of having the electron density and evaluated charge populations located on ions and their dependence on ion−ion separation. We found a sizable charge transfer from the ions to the surrounding water molecules, which in the case of fluoride, but not lithium, decreased upon formation of the CIP. The methodology established here opens the path to AIMD simulations of pairing of more complex, biologically relevant ions.

COMPUTATIONAL DETAILS

We performed Born−Oppenheimer AIMD simulations within the canonical constant volume ensemble, employing periodic boundary conditions in a box of 12.6 × 12.6 × 12.6 Å containing one lithium cation, one flouride anion, and 64 water molecules using a time step of 0.5 fs. The temperature of 300 K was maintained using the canonical sampling through velocity rescaling (CSVR) thermostat with a time constant of 50 fs.[41] More specifically, we used the hybrid Gaussian and plane waves method (GPW), as implemented in the Quickstep module of the CP2K package.[42] The system was treated at the density functional level of theory, employing the BLYP[43,44] functional with the Grimme correction scheme[45] to account for dispersion interactions. Kohn−Sham orbitals were expanded in a Gaussian basis set (TZV2P MOLOPT for O, H, and F and DZVP-MOLOPT for Li),[46] and we employed the norm-conserving GTH pseudopotentials.[47] A cutoff of 400 Ry was used for the auxiliary plane wave basis set. Free-energy profiles were obtained as the PMFs by constraining the ion−ion distance and evaluating the mean force along this coordinate.[24]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Further computational details and benchmark calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pavel.jungwirth@uochb.cas.cz.

Present Address

§O.M.: Department of Chemistry, New York University, New York, NY 10003, U.S.A.

Notes

The authors declare no competing financial interest.

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