SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CM1405
STSM title: Modelling of the 35/37Cl quadrupolar NMR relaxation parameters of chloride anion in the ionic liquid 1-decyl-3-methyl-imidazolium chloride [C10mim][Cl]
STSM start and end date: 24/09/2018 to 08/10/2018
Grantee name: Dovilė Lengvinaitė

PURPOSE OF THE STSM:

The aim of this STSM is to continue the collaboration project between molecular modelling groups at University of Cagliari and Vilnius University concerning the development of an efficient computational procedure to compute electric field gradients on quadrupolar anions in the 1-decyl-3-methyl-imidazolium chloride, [C10mim][Cl] ionic liquid. We have agreed on the following work plan
before the STSM:
1. To perform a series of DFT based test calculations to find a cost-effective yet reliable computational scheme for the calculation of the electric field gradients on the quadrupole nuclei of the chloride anions.
2. The effect of the second and further solvation shells on the electric field gradients of the anion will be evaluated. For this purpose, a suitable classical force field is to be selected to be used in the QM/MM calculations of the electric field gradients. The effect of the polarizable potentials will be investigated.
3. Computed $^{35/37}$Cl quadrupole coupling constants are to be compared to the available experimental data.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

An extensive series of DFT based test calculations of electric field gradient on the ^{35}Cl nucleus of the chloride anion in aqueous solution have been carried using different basis sets for water. The electric field gradients on the chloride anion generated by water molecules were analyzed. These calculations are primarily aimed to find a cost-effective basis set for reliable calculations of the electric field gradients on the quadrupole nuclei of the chloride anions. The test system is small enough and allows using very extensive basis sets.
A large discrepancy between the electric field gradients on chloride in the [C10mim][Cl] ionic liquid computed using purely classical approach and the combined QM/MM model was previously seen. In order to dissect this discrepancy, we have performed a series of test calculations on selected molecular samples by using different QM/MM approaches.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Nuclear quadrupole coupling constant of chloride is very sensitive to the structure of its nearest molecular environment, molecular species in the first solvation shell of the anion have to be described quantum mechanically. However, the promotion of the large C10mim cations to the QM region is met with huge computational burden. To perform a reliable computational scheme for the calculation of the electric field

gradients on the quadrupole nuclei of the chloride anions, we have previously considered computationally simpler system of aqueous solution of NaCl. We have selected the PBE0 exchange-correlation functional and aug-cc-pCVDZ basis set for Cl anion to be used in the QM/MM calculations of electric field gradients (EFGs) based on our previous experience. In previous work, we have seen that basis set of reasonable quality has to be used for water molecules in the first solvation shell. However, calculation with such basis set has been proven computationally too expensive in our calculation of the EFG when chloride anion is solvated by the C10mim cations. Therefore, we have checked the capabilities of other cost-effective basis sets. We have performed QM/MM calculations varying different basis sets for water when 7 water molecules nearest to the chloride are treated quantum mechanically. The test calculations have shown that the 6-31++G** basis could be considered as a compromise between accuracy and computational burden for the calculation of the electric field gradient in the ionic liquid systems. Basis sets for water molecules as large as Pople type 6-311++G(3df,3pd) or Dunning type aug-cc-pVDZ were seen to give reasonably converged results for electric field gradient on the chloride anion. However, these basis sets are clearly too large to be used in the QM/MM calculations of electric field gradients in the [C10mim][Cl] ionic liquid where several cations and anions amounting to 100-200 atoms in total might be needed to be described quantum mechanically and many configurations should be taken into account to obtain a reliable average to be compared to the experimental data.

The previous analysis of the MD trajectory of the [C10mim][Cl] ionic liquid has shown that chloride anion is coordinated by the C10mim cation in various ways. The Sternheimer approach based calculations of the nuclear quadrupole coupling constant of chloride anion revealed that this quantity is highly sensitive to the structure of the first solvation shell of the ion. The QM/MM calculations treating only the selected chloride anions quantum mechanically have shown that the computed electric field gradients can differ from those based on the Sternheimer approach significantly. The effect of the ionic liquid solvation shells on the electric field gradients of the selected chloride anions have been evaluated. For this purpose, we have performed calculations of electric field gradient of the selected chloride anions using different QM/MM approaches. First, we have performed ordinary QM/MM calculations by describing only single anions by the exchange-correlation functional, while the rest of the system was described by the point charge based force field. These calculations were supplemented by a similar set of calculations where the QM region was expanded by including 1 to 4 molecular species closest to the central anion, describing the rest of the system by point charges as before. Next, we have performed calculations where we have included only few closest molecules to the central anion with the rest of the system discarded. These closest molecules were described either classically or quantum mechanically.

The results of calculation just described allow to draw a few conclusions. We have found that to obtain more reliable results, molecular species in the first solvation shell of the anion have to be described quantum mechanically. However, the second and further solvation shells still generate electric field gradient on the chloride anion which is sizable and cannot be discarded. This is in contrast to the case of ordinary solutions where only the first solvation shell is typically seen to be responsible for the electric field gradient felt by the ion. The comparison between our QM/MM results for electric field gradients and those based on the classical Sternheimer approach raises some doubts concerning the validity of current Sternheimer factors for ionic liquid systems.

FUTURE COLLABORATIONS (if applicable)

The visit allowed to greatly advance the current project, and the collaboration will be continued extending the QM/MM calculations to a largest set of coordination geometries, necessary to compare the QM/MM results to the experimental ones. From a more general perspective, the results obtained, together with the currently available computational resources, indicate the necessity to evaluate also in other systems the validity of the use of Sternheimer factor to reproduce the effect of the electron cloud on the electric field gradient at the atomic nuclei.