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Prediction of the conductivity and compatibility of the selected ionic liquids (ILs) with Nafion™ using COSMO-RS

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Abstract. Proton exchange membrane (PEM) electrolysis is one of the waters splitting techniques available for producing green hydrogen. As such, improvement of the membrane ion conductivity will result in improvement of hydrogen production. Ionic liquids have recently been reported to enhance ionic conductivity of PEM. Herein, a screening method to select suitable ionic liquids for the development of efficient proton exchange membrane. COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS) was used to predict the ionic conductivity as well as the compatibility of the ions with the Nafion™ through the interpretation of σ-profile as well as interaction energy of the selected cations and anions. It was found that the anions namely of trifluoromethanesulfonate and nitrate with the cation of ammonium and imidazolium may be the best candidate for the ILs to be incorporated to Nafion™ for polymer electrolyte membrane (PEM) as the combination gives high ionic conductivity with considerable high interaction towards Nafion™. It is to be highlighted that the ionic liquids mainly interact with Nafion™ through the anion as implied by the high interaction energy of the anion towards Nafion™ compared to the cation.

Introduction

It is recorded in the Global Energy Statistical Yearbook 2022 that the domestic consumption of electricity in the Asia region for 2021 is 12,165 terawatt-hours (TWh)[1] pinpointing the demand for electricity that keeps on rising over the years. At present, coal remains the main source to generate electricity globally. Not only it is a non-renewable source, the usage of coal to generate electricity has contributed to greenhouse gas production. Due to this, it is of paramount importance to make use of a better option which is a renewable source. Hydrogen source for power generation particularly green hydrogen is an attractive choice of source as no greenhouse gas (GHG) is being released and with no carbon footprint as the only byproduct that is released through the process is water vapor [2].

Proton exchange membrane (PEM) electrolysis is one of the waters splitting techniques available for producing green hydrogen. The advantage of the techniques lies in the ease of fabrication where the PEM electrolyzer can be built according to the desired system. The most commonly used membrane for hydrogen production is perfluorosulfonic acid (PFSA) polymer membrane particularly Nafion™ due to its good ionic conductivity and excellent physicochemical properties [2, 3]. The former properties are vital as a high ionic conductivity is required to have efficient hydrogen production. The inclusion of ionic liquids (ILs) into the membrane is also another way to achieve this. The presence of ILs is reported to improve the proton conductivity of the membrane. The ionic liquids composed of cations such as ammonium, imidazolium, and

triazolium with a variety of anions such as tetrafluoroborate, chloride, trifluoromethanesulfonate, formate and nitrate have been reported to improve the conductivity [4-14].

As there are up to at least a million possible of ionic liquids due to various combination of cations and anions available, a prior prediction must be done to look for suitable ILs to be included in the membrane. COSMO-RS is a versatile tool for predicting the thermophysical properties of pure or mixed fluids. COSMO-RS which is based on quantum chemical calculations using the molecular structure and confirmation information can be used to gain a better understanding of the behavior of a molecule. In this study, COSMO-RS was used to predict the ionic conductivity as well as compatibility of ILs with the Nafion™ through the interpretation of σ-profile as well as interaction energy prediction of the selected cations and anions.

Methods

Structure optimization generation of the σ-profile, of the cations, anions, and Nafion™ structure

The method to optimize the structure in this study is adapted from [15-22]. COSMO-RS was used to determine the σ-profile of a molecule by performing quantum chemical calculations using molecular structure and confirmation information. The sigma (σ) profile can be defined as a probability of surface charge distribution on a molecular surface. To generate the σ-profile and σ-surface, T-Molex version 21.0.0 was used to optimize the structure of cations and anions at the DFT level. Firstly, the 3D molecular structure of the target molecule was built. The step was then followed by the geometry optimization through DFT calculation using parameterization of B3LYP with triple –ξ valence polarized basis set (TZVP). The optimized structures were then exported to COSMOthermX version 19.0.4 where the σ-profiles and σ-surface of the structures were generated.

COSMO-RS ionic conductivity prediction

The resulting optimized structures that were in form of COSMO file was used as the input in COSMO-RS to predict the properties of ionic conductivity of different combination of anions and cations at room temperature. The ionic conductivity (x=κ) is determined by equation (1):

$$\ln (x(T)x_0) = d^* + e^*(\ln(r^*_m)) + f^* (\ln/\sigma)) + E_{diel} /E_{diel0} + g^* (E/(RT)) + i^* (E_{diel}(T_0))/(R^*T^2) + d \quad (1)$$

where the field without the dielectric, $E_{diel\,0}$ = 1 kJ/mol, initial temperature, T_0 = 1 K. The term r^*_m is molecular radius, σ is symmetry number and R is gas constant. For ionic conductivity the regression parameter values are d= 8.784179, e= -15.668627, f= -1.141751, g= 0.025274, h= -0.054461 and i= 19.107936. The parameter values were obtained through the correlation of the experimental data to develop the model.

Estimation of the interaction energy of ions pairs of ionic liquids towards Nafion™

COSMO-RS was further used to estimate the ion interaction energy towards Nafion™ in which the Nafion™ and the ionic liquid molecule were treated as an equimolar mixture. To simplify quantum chemical calculation of the Nafion™ polymer, a dimer structure of two repeating units is used to represent the Nafion™ in this study as shown in Figure 1. The interaction energy namely misfit (E_{MF}), hydrogen-bond (E_{HB}), and van der Waals (E_{vdW}) were quantified using Equations (2), (3), and (4) respectively. Equation (5) on the other hand is the total interaction energy (E_{INT}).

$$E_{HB} = \alpha_{eff} c_{HB}\, min(0;\, \sigma_{donor} + \sigma_{HB}) \times max\,(0; \sigma_{acceptor} + \sigma_{HB}) \quad (2)$$

$$E_{MF} = \alpha_{eff} \frac{\alpha}{2} (\sigma + \sigma')^2 \quad (3)$$

$$E_{vdW} = \alpha_{eff} (\tau_{vdW} + \tau_{vdW}') \quad (4)$$

$$E_{INT} = E_{MF} + E_{HB} + E_{vdW} \quad (5)$$

Where α_{eff}, c_{HB} and σ_{HB} denote the effective contact area, the degree of hydrogen bond, and the lower limit of hydrogen bond respectively; σ_{donor}, and $\sigma_{acceptor}$ are the screening charge densities of hydrogen bond donor and acceptor, respectively; σ and σ' represent the screening charge densities of two different parts; τ_{vdW} and $\tau_{vdW}{}'$ are the specific van der Waals interaction parameter for each element.

Results and Discussions

COSMO-RS is a model to screen ionic liquids with specific properties. It can predict physicochemical properties such as viscosity and ionic conductivity henceforth helping the selection process of potential ionic liquids to be done effectively. This allows to leverage in terms of cost as it will avoid unnecessary synthesis reactions taking part as the properties of the ionic liquids can be predicted beforehand. Nevertheless, it should be bear in mind that, COSMO-RS merely serves as a tool to give a prediction of the physicochemical properties of an ionic liquid. The data predicted served as a guideline to narrow down the overwhelming number of simple ionic liquids. Hence, it is necessary for the prediction to be followed by experimental work [15-19].

The key properties for an ideal IL to be incorporated in the membrane for PEM is its ionic conductivity [4, 8]. The selection of the cation and anion was based on the previously incorporated ILs into the membrane of the Nafion™. In this study, the combination of the cations of imidazolium, boronium, ammonium, and phosphonium (Figure 2) with the anion of nitrate, tetrafluoroborate, formate, and trifluoromethylsulfonate (Figure 3) were predicted. The conductivities of the different combinations of anions and cations are summarized in Figure 4. Apart from that, the length of the alkyl chain of the imidazolium was also varied.

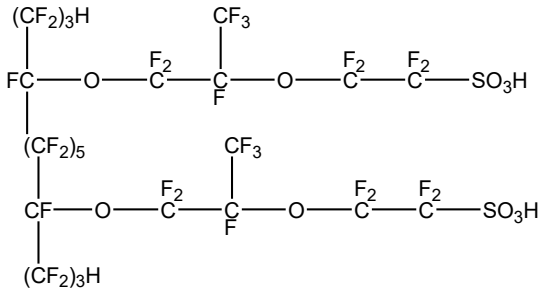

Fig. 1. Nafion™ dimer

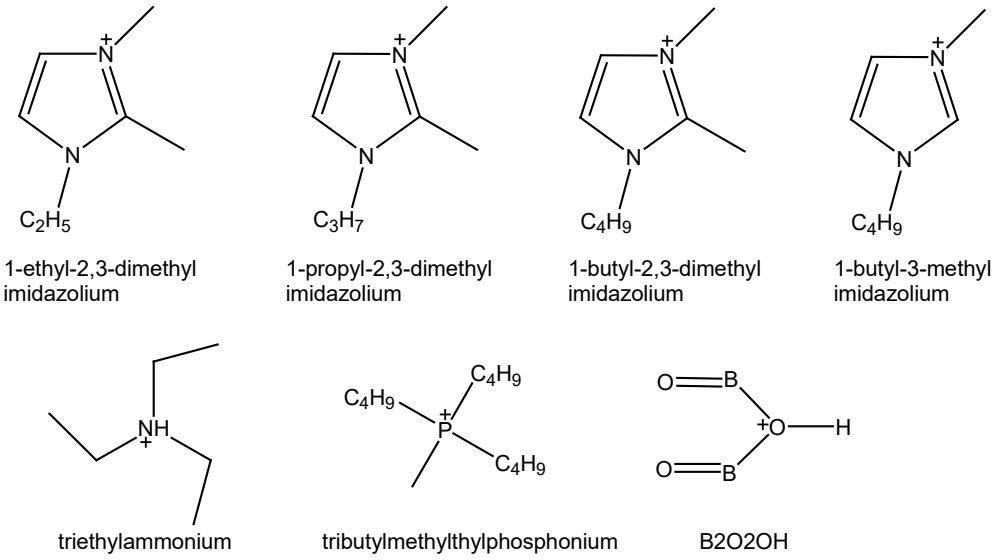

Fig. 2. Different cations structures of the ILs used in this study

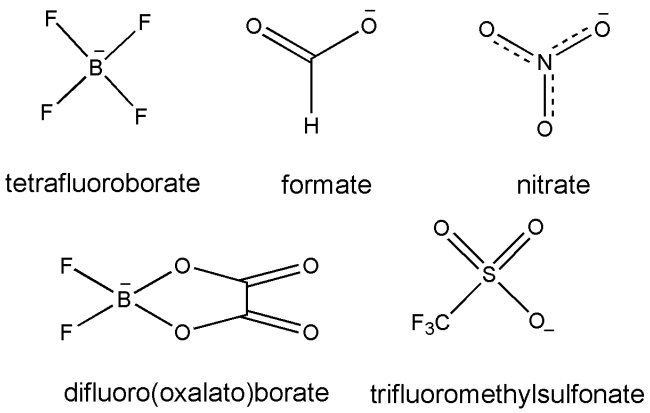

Fig. 3. Different anions structures of the ILs used in this study.

Based on the predicted conductivities, the variation of the anion has a greater effect on the ionic conductivity of the resulting ILs [18, 23]. The combination of nitrate anion followed by trifluoromethanesulfonate with all cations has resulted in the highest conductivity compared to other anions. This is in accord with the study reported in [12] where the incorporation of nitrate-based ILs into the Nafion™ membrane has resulted in a greater conductivity of the membrane compared to the usage of formate-based ILs. The variation in length of the alkyl chain attached to the imidazolium-based showed that the longer alkyl chain caused the ionic conductivity to be lower as it induced greater intermolecular attractions and impedes ion mobility as reported in [18, 23-26]. The phosphonium and boron-based ILs showed significantly lower conductivities compared to the imidazolium and ammonium-based ILs. This explains the prominent usage of imidazolium and ammonium cation-based ILs to improve the conductivity of the proton exchange membrane such as Nafion™ as reported in quite a significant number of studies [4-9, 11-13, 27-30].

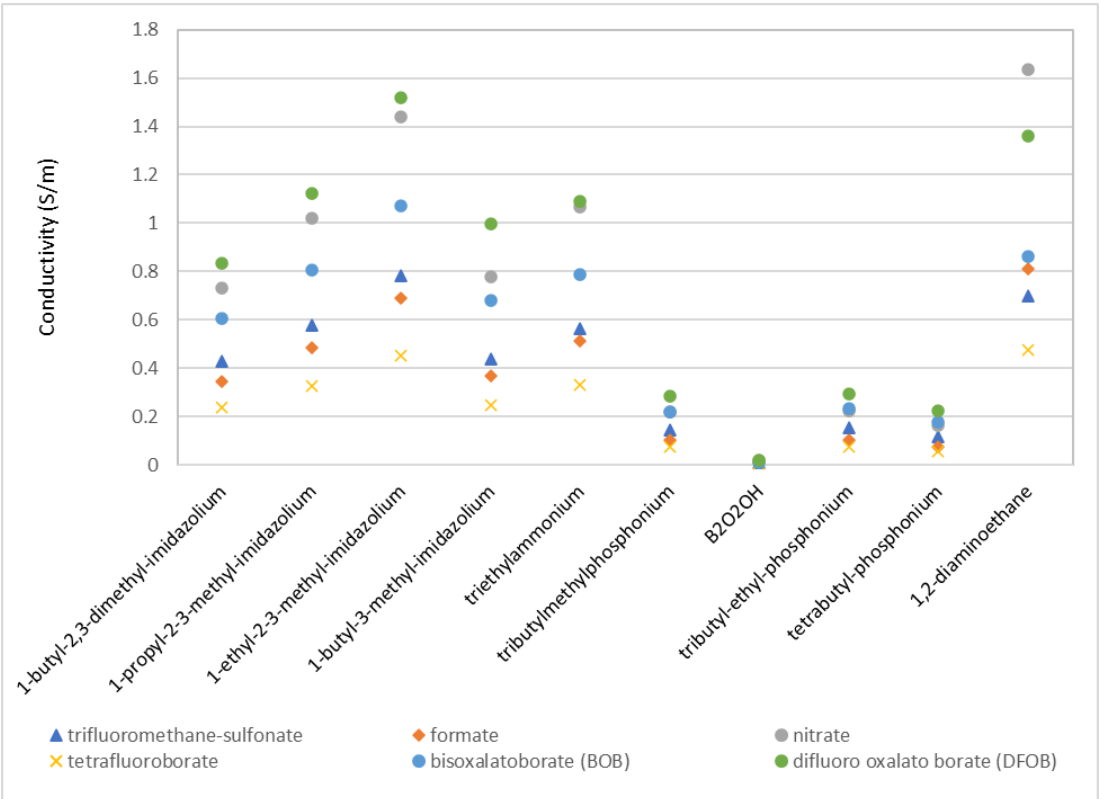

Fig. 4. Predicted conductivities of the cations and anions included in the study

The incorporation of σ-profile probability distribution in this study aids in explaining the compatibility of the cations and anions towards Nafion™. There are three different regions in a graph of σ-profile distribution that represents the nature of a molecule namely hydrogen bond donor (HBD), hydrogen bond acceptor (HBA), and nonpolar (NP) region [15-18]. The σ-profile probability distribution of Nafion™ is mostly nonpolar and with a very slight hydrogen bond acceptor in nature. This is attributable to the repeating fluorinated backbone unit (Figure 5). The σ-profile of the anion showed the compatibility of the anion namely nitrate, formate and triflate, with Nafion™. All three have σ-profile probability distribution in the non-polar region. The non-polar molecule has great affinity towards the non-polar molecule [17, 18] suggesting the compatibility of the anions with the polymer. Moreover, the slight distribution of σ-profile of Nafion™ in the hydrogen bond donor region may add up to the affinity of the three anions namely nitrate, formate and triflate, towards Nafion™ that are mostly of HBA in nature.

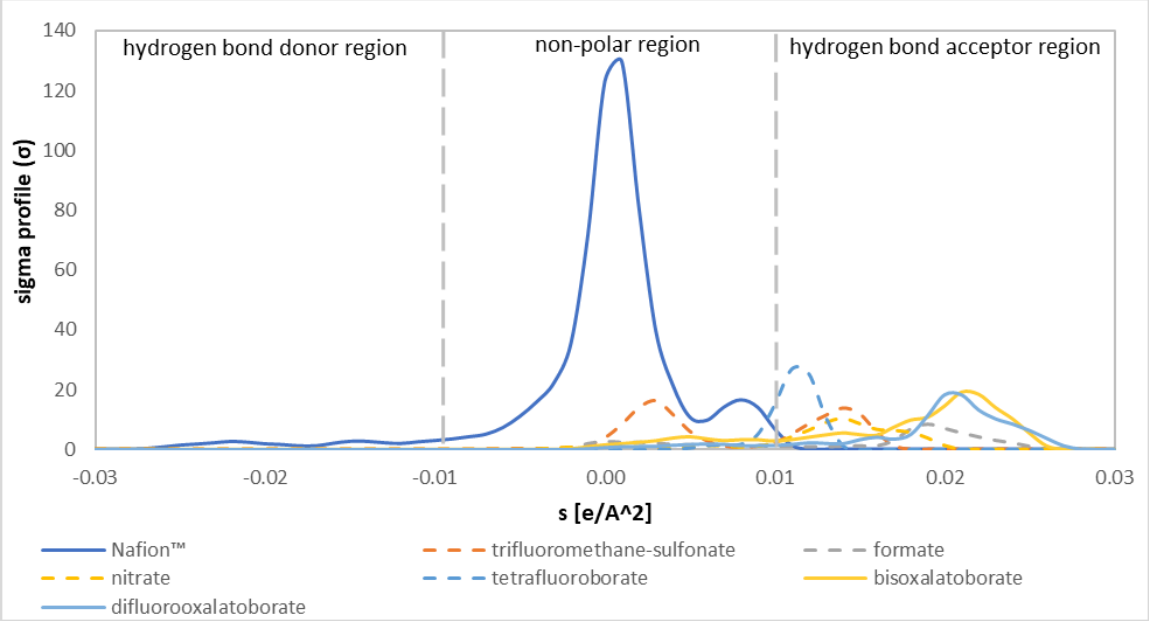

Fig. 5. Sigma profile distributions of Nafion™ and anions included in the study

As for the cation, the cation boronium and phosphonium may have a great affinity towards the Nafion™ structure as their σ-profile distributions are mostly in HBA in nature for the former and partially HBA and non-polar in nature for the latter (Figure 6). On the other hand, the cation, imidazolium, and ammonium may interact to the Nafion™ molecule through their nonpolar area of the cations as their σ-profile distributions mainly are in the nonpolar region.

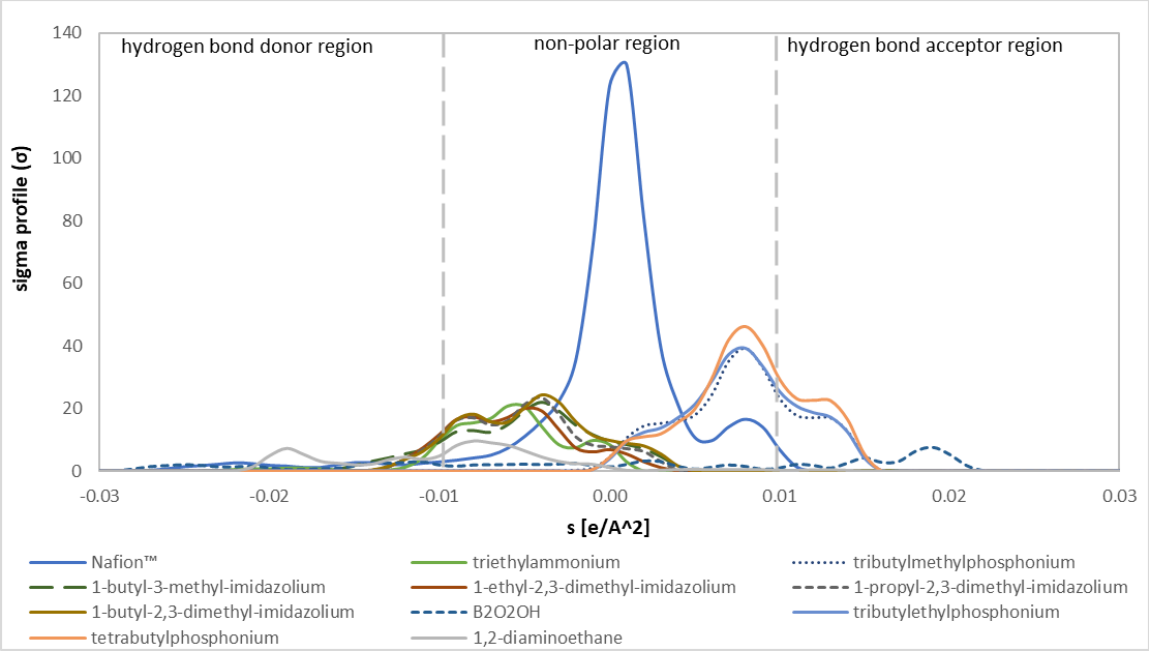

Fig. 6. Sigma profile distributions of Nafion™ and cations included in the study

The COSMO-RS was further used to predict the interaction energy of the ionic liquids towards Nafion™. The effect of the anion and cation was individually assessed. In the decreasing order, the interaction energy of the anions (kcal/mol) is formate > nitrate > trifluoromethane-sulfonate > tetrafluoroborate (Figure 7). If we correlate the data with the σ-profile, the nature of the formate anion that has the greatest HBA character among the anions included in this present study has caused the interaction energy of formate towards Nafion™ to be the highest. This also suggested the mode of interaction of the ILs towards the Nafion™ dimer is through the anion. Although the distribution of the σ-profile of the Nafion™ molecule is highly concentrated at the non-polar region attributable to the fluorinated backbone but the main mode of the interaction between the anion and the molecule is through the acidic area of the molecule that is the sulphonic acid group.

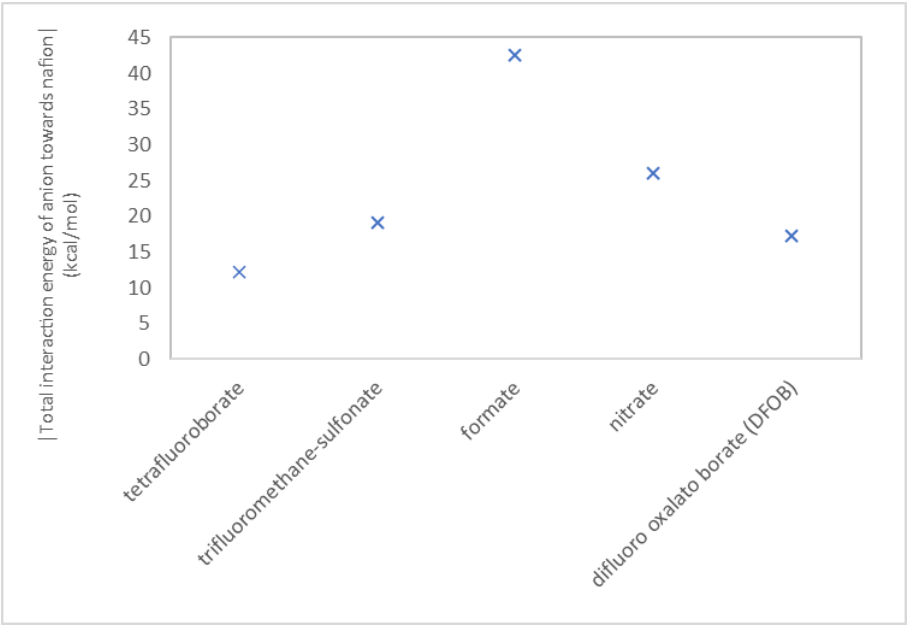

Fig. 7. Interaction energies prediction of anions included in the study towards Nafion™

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This is further supported by the interaction energy of the cations. The boron-based cation that has the highest affinity towards the Nafion™ has the most prominent distribution in the HBA region pinpointed the main interaction of the cation towards the Nafion™ molecule is through the HBD area (Figure 8). As such, the interaction of phosphonium towards the Nafion™ is the second highest after boronium as the distribution of phosphonium cation lies partially in HBA and non-polar. The cation of imidazolium and ammonium showed slightly lower interaction energy compared to the phosphonium cation in which the mode of interaction of the cations is through the alkyl chain of the cations that contributed to the non-polar nature.

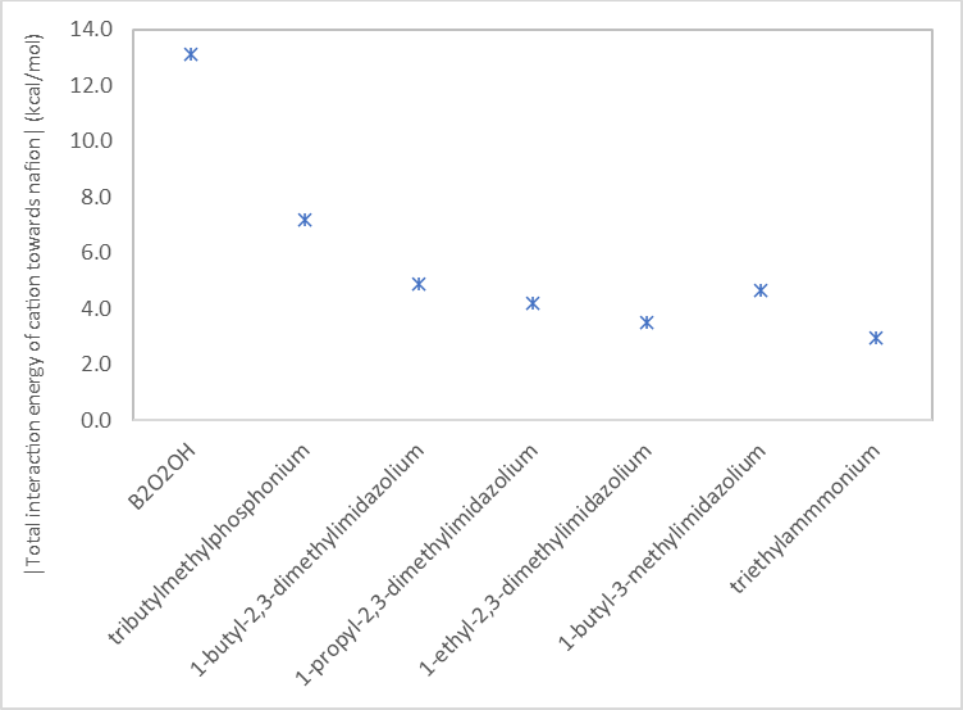

Fig. 8. Interaction energies prediction of cations included in the study towards Nafion™

Conclusion

The combination of imidazolium and nitrate anion gives out the best conductivity followed by the combination of the same cation with trifluoromethanesulfonate. The σ-profile showed the non-polar nature of the Nafion™ dimer. The imidazolium and ammonium cation lies mostly in the non-polar region whilst boronium and phosphonium have some distributions in the hydrogen bond acceptor region. The interaction energy suggested that the main interaction of the ionic liquids is through the anion as the anion has significantly high interaction energy towards the Nafion™ compared to the cation. Furthermore, as the anions are hydrogen bond acceptor in nature and has high affinity towards hydrogen bond donor, this revealed that the main interaction mode of the Nafion™ is through the sulfonic group that contributed to the HBD nature of the polymer. Taking into consideration the prediction through COSMO-RS, the anion of trifluoromethane sulfonate, nitrate with the cation of ammonium and imidazolium may be the best candidate for the ILs to be incorporated into Nafion™ for polymer exchange membrane (PEM) as the combination gives considerably high ionic conductivity with considerable high interaction towards Nafion™. This result may act as the basis for the selection of suitable anions and cations to be incorporated into Nafion™ experimentally.

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