Molecular Dynamic Simulation of Dielectric Constant of Organic Electrolyte Tetraethylammonium Tetrafluoroborate in Solvent Acetonitrile

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Abstract: ***Stable and efficient organic electrolytes have become a critical need in recent energy devices and technology. One*** **main characteristic of electrolyte that affects the electrolyte performance is the dielectric constant (ε). Several mixture equations have been suggested to calculate the dielectric constant mainly for the solid binary composites. In this work we have estimated ε for the organic electrolyte tetraethylammonium tetrafluoroborate (TEABF4) in solvent acetonitrile (AN). The theoretical estimation of ε is done using weighted average (WA), complex refractive index (CRI), Looyenga, and effective medium approximation (EMA) mixing rules. Out of the mixing rules EMA has only approximated the increase in ε with volume fraction of TEABF4, but it has shown a sharp increasing nature. The molecular dynamics (MD) simulation is performed in NVT ensemble using open-source code LAMMPS. The fluctuation theory has been used to estimate the polarizability (P) and ε for 2.8 M composite. The MD simulation is showing a high value of ε (= 94). A large value of dielectric constant is often desired for electrolytes, the organic composite consists of TEABF4 in AN may be a sustainable and better choice for future energy devices.**

Keywords: Energy Material, Organic Electrolyte, Mixture equations, Molecular Dynamics, Dielectric Constant.

INTRODUCTION

Energy materials are substances used for energy storage, transmission, and conversion, and they play a vital role in improving efficiency and reducing power consumption in devices such as batteries, dry cells, and super capacitors. The key component in these systems is the electrolyte, which dissociates into ions and enables electrical conduction, thereby determining the stability, conductivity, and efficiency of energy storage devices. Traditionally, many energy materials are inorganic composites, but they present challenges related to disposal, renewability, pollution, and sustainability. To address these issues, research has shifted toward renewable and eco-friendly materials, with organic electrolytes gaining attention due to their wide electrochemical stability window and compatibility with carbon electrodes. Systems such as tetraethyl ammonium tetrafluoroborate ($TEABF_4$) dissolved in polar solvents like propylene carbonate (PC) or acetonitrile (AN) are widely studied in electrochemical double-layer capacitors because they offer high ionic conductivity and stability.

A central property influencing the performance of electrolytes is the dielectric constant (ε), which describes how a material responds to an electric field. It governs ion dissociation, solvent polarity, and electrostatic screening, with higher dielectric constants promoting more free ions and improved conductivity. However, in concentrated solutions, ε decreases due to strong ion–solvent coordination and limited molecular reorientation, reducing conductivity. In mixtures, the dielectric constant does not vary linearly with composition but depends on volume fraction, molecular interactions, and the inherent dielectric properties of the components. Understanding and predicting ε is therefore crucial for designing high-performance and sustainable energy materials.

Since direct experimental determination of dielectric constants in concentrated organic electrolytes is challenging, molecular dynamics (MD) simulations have become a powerful tool to study dielectric behavior at the atomic scale. The present project focuses on two main objectives: first, to review theoretical models used to estimate the dielectric constant of binary mixtures such as $TEABF_4$ with acetonitrile, and second, to employ molecular dynamics simulations to investigate the dielectric response of $TEABF_4$ in AN solvent. This combined theoretical and computational approach provides insights into the behavior of organic electrolytes, paving the way for the development of eco-friendly and efficient energy storage systems.

Alta Fang and Alex Smolyanitsky [1] studied the electric double-layer capacitors performance is very sensitive to the electrolyte used and electrolytes made of ionic liquid mixtures have been found to have potential in facilitating high energy densities. In this case all-atom molecular dynamics simulations of ionic liquids with 1-ethyl-3-methylimidazolium and tetrafluoroborate are conducted, together with planar sheets of graphene as electrodes. We show that relative ion-electrode van der Waals interactions are significant to the population of ions adsorbed to the first interfacial layer to the electrodes that are not charged. Yi-Jung Tu et al [2] examined constant potential molecular dynamics simulations to determine the correlation between capacitance and interfacial structure of supercapacitor systems made using pristine graphite electrodes along with a series of organic solvents and [BMIm+] [BF_4^- -] / acetonitrile electrolytes at different concentrations. Xuewen Fu et al [3] are works that Microwave dielectric ceramic materials are widely applied in microwave applications due to their high dielectric and quality factors. These applications also need zero temperature coefficient ceramics at the resonant frequency (0) and can be implemented either by blending a ceramic of interest with a different ceramic or by carrying out the ionic substitution.

Andrzej and erkoandpeiming [4] remarked that a general model has been worked out to compute the statical dielectric constant of mixed-solvent electrolyte solutions. In mixtures of solvents without components of electrolytes, the model is developed on an empirical correction of the Kirkwood theory for multi component systems. In the case of systems with electrolytes, the model

considers calculate the influence of ions and ion pairs and, thus, can reproduce the dependence of the dielectric constant on electrolyte concentration. Daniel Pabsch, et al [5] explained that of special interest to industry is salt solubility in organic solvents, such as carbon capture and storage or utilization processes, battery technology, or biotechnology. Electrolyte thermodynamic models have been established to minimize experimental work to design an electrolyte to desired properties, such as, high solubility in an organic solvent. Mengjie et al [6] indicated that redox-active polymers and small organic compounds organic batteries have proved to be the most promising ones in next-generation energy storage devices because of the plenty of organic resources, their environmental friendliness and versatility. Up to now, enormous research has been dedicated to creation of improved organic electrode materials and the correlation between the material structure and the performance in organic batteries. Chaoyue Wang et al [7] state that the dielectric constant of the four biomass materials is not lower than that of starch and lignin, and are positively correlated to their cellulose content. Dielectric loss factors of all these biomass materials were lower than one. This work will offer a novel method of measuring the dielectric properties of the biomass materials and other porous media materials that have complicated structures. Lidan et al [8] that A modified rule of mixtures was put forward to predict their mechanical and dielectric properties. This paper provides an insight on how to develop nanofiller incorporated cement-based materials with improved mechanical and dielectric properties. Michiel Sprik [9] stated that the static dielectric constants of a variety of water models are compared. These models share the fact that each of them provides a good description of the dynamics and geometry of the hydrogen bonding in the liquid. The work by Ramesh et al. [10] explained particular, TEABF4/AN systems were studied and a systematic decrease of the dielectric constant was reported with increasing salt concentration. Their MD simulations indicated the molecular basis for this reduction: restricted molecular orientation of PC molecules and the formation of TEA^{+}-BF^{-} ion pairs.

In this work we have estimated the ε of the TEABF4 in solvent AN and PC using some of the well-known and relevant mixing rules theoretically. Determination of ε of concentrated electrolytes especially of organic electrolytes are difficult experimentally. Thus, to estimate the correct value of dielectric constant of TEABF4 in solvent AN molecular dynamics computer simulations are performed. In this work we reviewed some existing theoretical rules to estimate dielectric constant of binary mixture of organic electrolyte TEABF4 and solvent acetonitrile (AN), and we molecular dynamics simulation to examine the dielectric constant of TEABF4 in solvent AN.

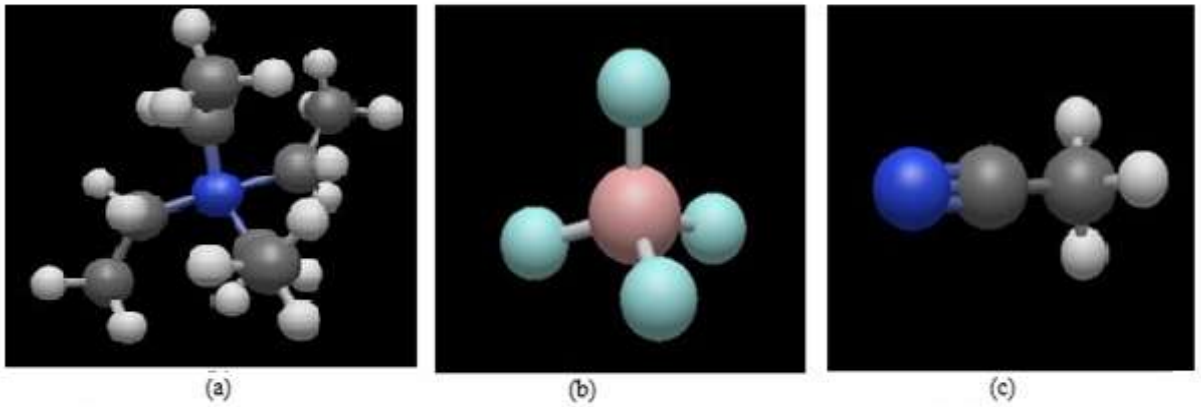

Fig-1: Optimized geometry of (a) Tetraethylammonium (TEA^{+}) ligand (b) Tetrafluoroborate (BF_{-}^{4}) ion and (c) Acetonitrile (AN)

THRORETICAL DESCRIPTION

Estimating the dielectric constant of a binary composite with various mixing rules are very popular among researchers for many years. Finding the fittest model that estimate the dielectric constant of binary composites showing good agreement to the experimental data is a common approach. The mixture equations we have used to calculate dielectric constant of TEABF4 in solvent AN is described below.

Linear Rule of Mixtures (Volume-Weighted Average)

Assumes a simple linear interpolation based on volume fractions.

$$\varepsilon_{eff} = f_1\varepsilon_1 + f_2\varepsilon_2$$

f_1, f_2 be volume fractions
ε_{eff}: effective dielectric constant of the mixture
ε1, ε2: dielectric constants of materials 1 and 2.

Lichtenecker's Logarithmic Rule

A semi-empirical rule that often gives better agreement with experiments
$log\ (\varepsilon_{eff}) = f_1 log(\varepsilon_1) + f_2 \log(\varepsilon_2)$
Applicable to a wide variety of mixtures including random distributions.

Maxwell-Garnett Approximation (Effective Medium Theory)

Used for dispersed systems (e.g., spherical inclusions in a host matrix).

$$\varepsilon_{eff} = \frac{\varepsilon_h\left(\varepsilon_i + 2\varepsilon_h + 2f(\varepsilon_i - \varepsilon_h)\right)}{(\varepsilon_i + 2\varepsilon_h - 2f(\varepsilon_i - \varepsilon_h))}$$

ε_h: dielectric constant of the host matrix
ε_i: dielectric constant of the inclusions
f: volume fraction of inclusions

Looyenga's Formula

Empirical model that's often accurate for mixtures with moderate contrast in permittivity.

$$\boldsymbol{\varepsilon_{eff}^{1/3} = f_1\varepsilon_1^{1/3} + f_2\varepsilon_2^{1/3}}$$

There are many other formulas which are widely predicted by researchers and used for estimating the dielectric constants of binary equations.

Molecular dynamics (MD) simulation is a powerful computational method for studying the structural, dynamic, and dielectric properties of electrolyte systems at the atomic scale. The dielectric polarizability *P* and the dielectric constant ε are related as, $D = \varepsilon_0 E + P$

Dielectric polarizability *P* consists of the polar and nonpolar contributions, the nonpolar part of *P* is obtained from the molar density ρ_i, and the molecular polarizability α_i, of the components through the relation,

$$P_{non} = \frac{4\pi}{3} N_A \sum_i \alpha_i . \rho_i$$

The polar contribution to the dielectric polarizability *P* comes from the fluctuations in the total dipole moment of the ensemble of molecules. The quantity ε_{pol} is calculated from the MD simulation using the fluctuation rule considering the proper electrostatic interactions and hence finding long-time average value of the square of the total dipole moment $< M^2 >$. The fluctuation rule says that these small, random fluctuations are directly related to the macroscopic properties of the system (like heat capacity, compressibility, or dielectric constant).

$$\varepsilon_{pol} = 1 + \frac{4\pi < M^2 >}{3V k_B T}$$

Where: V= volume of the system
T = temperature
k_B = Boltzmann constant
$M^2 = (\sum_i \mu_i)^2$ where $\mu_i$is the dipole moment vector of molecule i.
<·> = average over time.

The polar part of the dielectric polarizability *P*, (P_{pol}) is expressed as, $P_{pol} = \frac{(\varepsilon_{pol}-1)(2\varepsilon_{pol}+1)}{9\varepsilon_{pol}}$

The total polarizability is then P = P_{non} +P_{pol} . The dielectric constant is obtained by solving the Kirkwood relation for ε, and we obtain the dielectric constant as,

$$\varepsilon = \{(1+9P)^2 + [(1+9P)^2 + 8]^{1/2}.$$

THEORETICAL RESULTS:

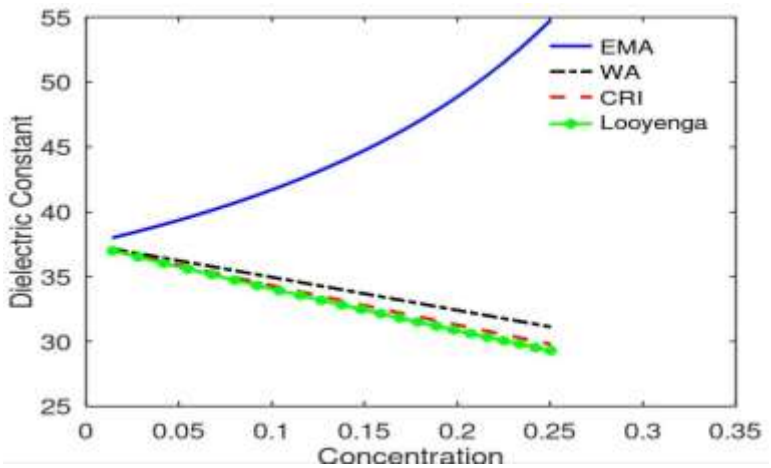

Fig-2: Dielectric constants of the electrolyte ($TEABF_4$) and solvent (AN) composite with variation of electrolyte concentration

Figure-1 shows the variation of the dielectric constant with concentration for an organic electrolyte–solvent mixture, based on different mixing rules.

- EMA (Effective Medium Approximation, blue solid line): Shows a strong nonlinear increase in dielectric constant with concentration. Starts around ~38 at zero concentration and rises steeply, reaching ~55 by concen-tration 0.3. This model predicts an enhancement effect, meaning the mixture dielectric con-stant grows significantly with solute concentration.
- WA (Weighted Average, black dashed line):Exhibits a linear decreasing trend. Starts near 37 and gradually decreases toward ~31 at concentration 0.25. Assumes simple volumetric mixing without strong interactions.
- CRI (Complex Refractive Index model, red dashed line): Similar to WA but slightly lower values. Starts at ~37 and decreases to ~30 at concentration 0.25. Suggests that the mixture has a reduced dielectric response compared to WA.
- Looyenga model (green line with markers):Closely follows the CRI trend. Decreases nearly linearly with concentration, reaching ~29 at concentration 0.25. This model accounts for a power-law type relationship in dielectric mixing and seems to align with CRI.

EMA predicts an increasing dielectric constant, unlike the other three models which predict decreasing trends. This indicates that EMA assumes stronger polarization effects from the solute, while WA, CRI, and Looyenga emphasize dilution or reduced permittivity. However, the EMA mixing rule is showing an almost exponential increase in dielectric constant with concentration. This type of sharp increase in dielectric constant is hard to describe. Hence, for liquid bio composites with dissimilar dielectric constant any of known rules is not providing satisfactory explanation and results. Therefore, details atomic and molecular level interaction study using simulation is a way to predict and understanding the dielectric constant of liquid bio composites.

MOLECULAR DYNAMIC SIMULATION

The binary mixture consists of $TEABF_4$salt and the organic solvent acetonitrile is simulated by MD calculation. The MD program package of LAMMPS is used in the present simulations.[11] The bending and torsion terms for the intramolecular interactions and the Lennard–Jones and Coulomb terms for the intermolecular interactions were taken into account by the potential function. QM calculations using CM1A-LBCC method are performed for these interactions and to obtain parameters in LigParGen [12]. The molecular structures of TEA+ legand, BF_4- ion and acetonitrile molecule are generated using Avogadro [13]. The internal geometries of each molecule are arranged as per the optimized structures and the atomic and molecular interaction parameters are generated by LigParGen based on the OPLS-AA force field. A cubic cell under a periodic boundary condition is assumed for the configured system. We placed 184 molecules consists of total 1544 atoms (144 molecules of acetonitrile, 20 TEA^+ ligands and 20 BF_4^- ions) in a cubic cell of 48 × 48 × 32 Å to obtain the initial system. The initial system is configured in Moltemplate.

The verlet method is applied to the integration with a time step of 1 fs. The electrostatic interactions were computed using the smooth particle mesh Ewald (PME) method with a cutoff distance of 10 Å. The temperature and pressure were controlled by NoseHoover and ParrinelloRahman methods respectively.

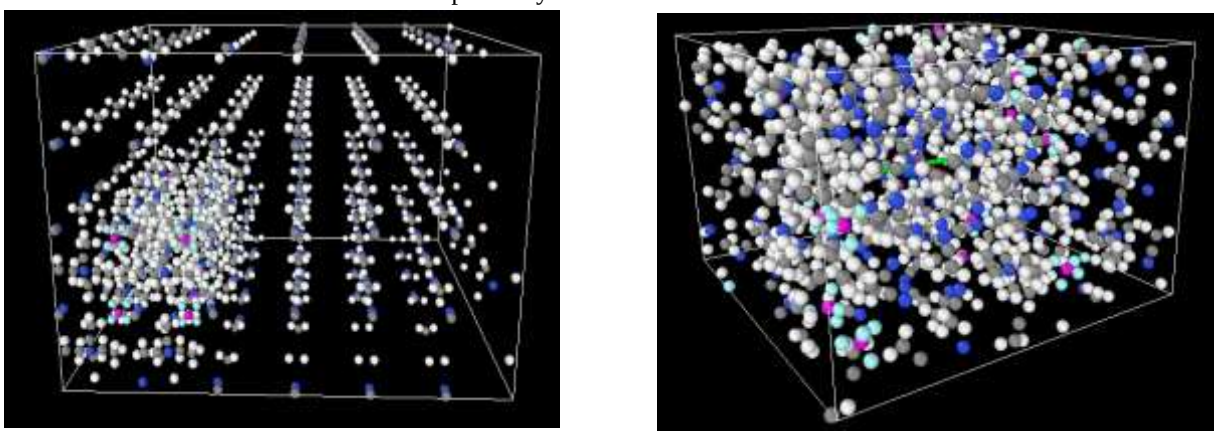

Fig-3: (Left) initial configuration and (righr) Equilibrium configuration of the 184 molecules arranged using Moltemplate in a box of dimension 48 × 48 × 32. Pink = Boron, Blue = Nitrogen, Dark gray = Carbon, White = Hydrogen, Cyan = Fluorine

A four-step equilibration process (expand, minimize, reorient and compress) is applied on the 1:2 $TEABF_4$ and AN binary mixture. In general, it is good to minimize the system first. The quick minimization and then steepest descent method was applied to minimize the energy of the system. The atomic positions in the configured system are randomized for a few thousand steps using langevin dynamics in NVE ensemble. Then the system is relaxed in NVT ensemble at temperature 323 K to enable the molecules to move freely and reorient themselves. The simulation box is considered large as compared to the number of atoms. Hence, the system is accompanied by NPT run for 0.9 ps at pressure 100 atm. Then the system kept at 300 K and 1 atom pressure (NPT) for another 0.5 ps to obtain the correct density of the binary mixture. The Nose-Hoover thermostat [14, 15] and the Berendsen [16] methods were used for controlling the pressure and temperature respectively. The Ewald summation was implemented using the particle mesh Ewald (PME) scheme. Calculation of long-range electrostatic interactions through fast Fourier transforms to handle the periodic boundary conditions of the configured system is done with LAMMPS k space style PPPM.

The equilibrated system is faded to the NVT ensemble simulation. The system is simulated in NVT for 10 ns considering E = 0 and D = 0 boundary conditions. The dipole moment of each molecule is calculated over last 5 ns of NVT simulation. Dielectric constant can be measured using fluctuation rule.

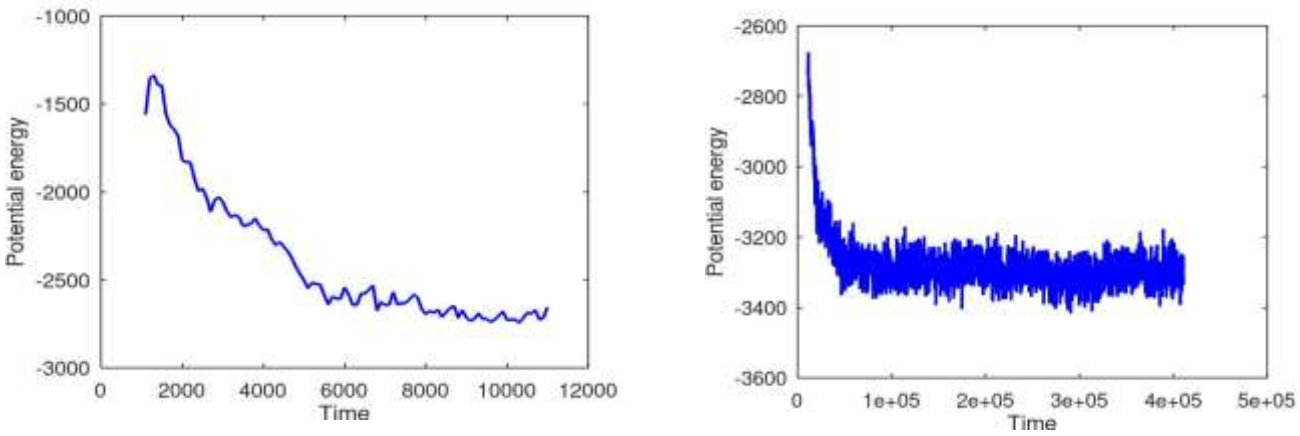

Fig-4: Potential energy vs time plot for equilibration of binary mixture (a) setting free all the molecules to rearrange themselves using Langevin dynamics in NVE at 323 K, (b) NVT equilibration at 323 K to obtain stable configuration.

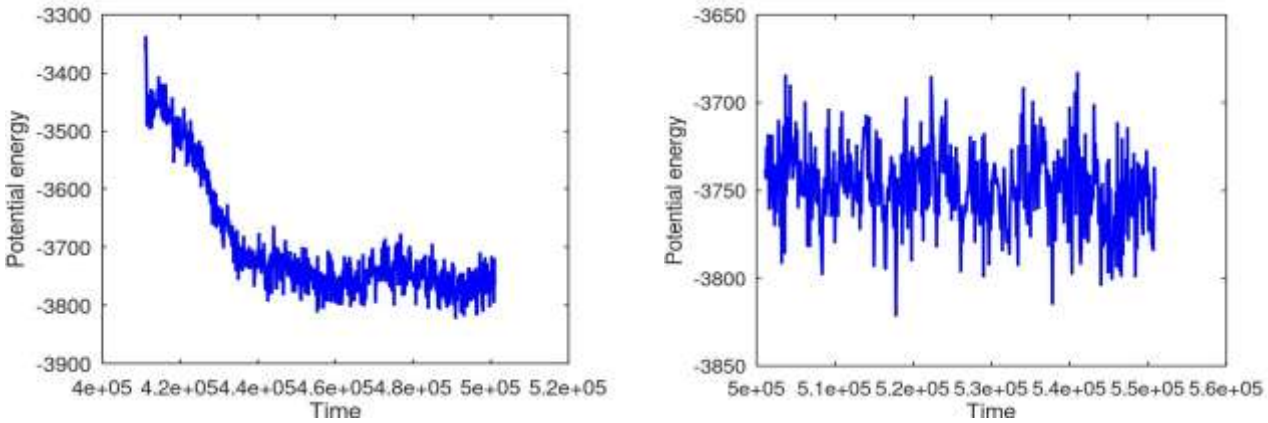

Fig-5: Potential energy Vs time plot for equilibration of binary mixture in NPT to obtain correct density (a) NPT equilibration at 300 K and 100 atm pressure, (b) NPT equilibration at 300 K at 1 atm pressure.

CONCLUSIONS

Efficient organic electrolytes have become one of the most important substances in recent energy devices and technology. One main characteristic of electrolyte that affects the electrolyte performance is the dielectric constant (ε). Dielectric constant also indicates the screening effect of the medium to electrostatic interactions and hence controls the degree of ion dissociation and ionic conductivity. An increase in the dielectric constant will increase the tendency of free ions, and a decrease will increase ion association at higher concentrations reducing conductivity. The dielectric behavior at the molecular scale with the electrochemical performance at the macroscopic scale, and confirms the need for comprehensive molecular-scale simulations to optimize electrolyte formulations for energy storage applications that are efficient, stable and sustainable.

Based on the experimental observations and best fitting to experimental data several mixture equations are suggested to calculate the dielectric constant of the binary mixtures. But these mixing rules are mainly designed for the solid composites. The Looyenga and EMA rules demand to be useful for liquid composites also, but the organic liquid composites are quite complex. We have tested WA, CRI, Looyenga and EMA mixing rules to calculate the dielectric constant for the organic composites consists of $TEABF_4$ salt in organic solvent AN and PC. It is clear from some of the other relevant works that the decrease of dielectric constant in binary composites for our considered composites is not acceptable. Hence, the result obtained from EMA mixture equation is somehow acceptable as it is showing an increase in the dielectric constant with increase in volume fraction of $TEABF_4$. Among the mixing rules tested, EMA obtains a sharp and monotonic increase in dielectric constant with solute volume fraction and WA, CRI and Looyenga display a decreasing trend. This deviation stresses the limitations of simple averaging-based rules for liquid bio-composites.

The inability of WA, CRI and Looyenga to reproduce the observed dielectric enhancement suggests that microscopic ion-solute and ion-ion interactions are necessary. EMA better characterizes the electrolyte by including local field effects, so that it is appropriate to model concentrated electrolytes. The EMA rule is approximating the value of dielectric constant to be 43.20 for $TEABF_4$ with a volume fraction 0.126735 in solvent AN (2.8 M solution).

The binary mixture consists of $TEABF_4$ salt and the organic solvent acetonitrile is simulated using MD simulation. The MD program package LAMMPS is used in this work. The simulation is performed for 2.8 M solution. We placed 144 molecules of acetonitrile, 20 TEA+ ligands and 20 BF4- ions in a cubic cell of 48 × 48 × 32 Å, maintaining the proper ratio of consisting molecules to obtain the molecular concentration of 2.8 M solution. The system is well equilibrated using four step (expand, minimize, reorient and compress) equilibration, after equilibration the molecular configuration is exposed to NVT ensemble for time evaluation for 10 ns. The dipole moment of each molecule is calculated 5000 times for last 5 ns. The polarizability and the dielectric constant are calculated for the 5000 samples using fluctuation rule. The calculated dielectric polarizability for 2.8 M mixture P is found 20.78 C m^{-2} and the dielectric constant is found 94. A large value of dielectric constant is often desired for electrolytes, the organic composite consists of TEABF4 in AN may be a sustainable and good choice for current energy devices and technology.

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