Studies on the interaction of Na\(^+\) ion with binary mixture of carbonate-ester solvents: A density functional theory approach

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Abstract. The advancement of sodium-ion batteries as an alternative to lithium-ion batteries presents a viable way to make energy storage cost-efficient. However, the inherent properties of Na\(^-\) are not quite well understood as it is for Li\(^-\), which also include solvation of Na\(^+\) in non-aqueous electrolyte for its application in electrochemical devices. Here, a comprehensive study of Na\(^-\) solvation in the binary mixture of ethylene carbonate (EC) and propylene carbonate (PC) in different ratios is reported, using density functional theory calculation. The optimised structure of cluster of binary mixture EC-PC-Na\(^-\) in three different ratios (1:1, 2:1 and 3:1) of EC: PC is analysed. Binding and Gibbs free energy of Na\(^-\) solvated by EC and PC and charge on Na\(^+\) is calculated. The calculated results favour the stability of binary mixtures containing higher concentration of ethylene carbonate. In infrared (IR) vibrational spectra, substantial changes are observed in the IR active modes of the solvent because of cation-solvent interaction.

1. Introduction
Ample amount of research is going on across the globe to encourage sodium-ion batteries (SIBs) as an alternative to lithium-ion batteries (LIBs) as an electrochemical energy storage device [1-2]. These efforts are being made not only to meet the dramatically increasing demands of sustainable resources but also to cut down the cost of electronic devices without compromising the high power density offered by LIBs [1,3]. SIBs are attracting tremendous attention because of their cost-effectiveness and comparable energy density as offered by LIBs [4-5]. Reason for a lesser rate of SIBs is the high sodium concentration in the earth's crust and oceans relative to lithium [6]. Generally, for understanding the fundamental of SIB materials, researchers in the field of sodium-ion batteries (SIB) make use of much know-how and examples from the field of lithium-ion batteries (LIB)[5]. A small but important aspect of these endeavours is modelling of electrolytic system via computer simulations to facilitate the exploration of the optimal electrolyte for SIBs [4,7]. Liquid electrolytes have always been the most widely used electrolyte for LIBs and therefore have gained attention for SIBs as well.
Particularly the most common carbonate ester and ether used as a non-aqueous electrolyte are the same for LIBs and SIBs [8]. Not only the solvents but also sodium salt is almost analogous to lithium [9,10]. “The changes in energies, enthalpies, and free energies for all steps in a number of possible reduction reaction of common carbonate solvents: ethylene carbonate (EC), propylene carbonate (PC), and vinylene carbonate (VC) with Na⁺ ion” has been studied by Liu et al [11].

Mehdi et al. [1] has already thoroughly addressed the solvation of Na⁺ and its solvation shell structure in a cluster comprising pure solvent molecules pertaining to its role in the formation of solid electrolyte interface. Conduction of Na⁺ cation in pure solvent and its binary mixtures was studied by Liu et al. [12]. It was observed that binding energy of binary mixtures was higher than for pure solvent containing clusters inferring the stability of binary mixtures and their better ion conduction capability. While the holistic study of a specific binary mixture in search of an optimal ratio of its constituent component to obtain the best ionic conduction is yet to be approached by density functional theory calculations [8].

In this work, the sodium ion solvation particularly in binary mixture of cyclic carbonates (EC and PC) in the different ratio is studied by DFT calculation. An understanding of the intrinsic characteristic of Na⁺ solvation in the non-aqueous electrolyte is provided through this work, which could directly affect the intercalation process at the electrode-electrolyte interface. This ultimately decides safety, lifetime and efficiency of SIBs. Systems of Na⁺ with increasing concentration of EC in binary mixture of EC: PC is stimulated to investigate the role of solvation shell in the non-aqueous electrolyte. Binding energy, Gibbs free energy, Mulliken charge and dipole moment has been calculated for nEC-PC-Na⁺ (1 ≤ n ≤ 3). For further investigation of systems, IR studies have also been carried out.

2. Computational Method
The density functional theory (DFT) calculations were performed in Gaussian-09 software package. B3LYP functional and 6-31G basis set was chosen to carry out the electronic and frequency calculations for the molecules under study [13]. The molecular structure of EC and PC are shown in Figure 1. The geometry optimisation of the cluster of binary mixtures of EC:PC in three different ratios (1:1, 2:1 and 3:1) complexed with Na⁺ ion was performed. The strength of the interaction between Na⁺ and EC: PC based binary mixture are assessed by calculating the binding energy of the formation of the nEC-PC-Na⁺ (1 ≤ n ≤ 3). For these ratios of binary mixtures complexes, the binding energy was calculated using Equation 1. Binding energy is defined as the difference between total electronic energy of the product and reactant [10].

\[
\Delta E = E_{[Na^+n(\text{PC})]} - [E_{Na^+} - nE_{EC} - E_{\text{PC}}] \tag{1}
\]

Where \(E_{[Na^+(\text{EC})_n(\text{PC})]}\), \(E_{[Na^+]}\), \(E_{[\text{EC}]}\) and \(E_{[\text{PC}]}\) represent the total energy of the molecule shown in their respective parenthesis. Similarly, using the equation below Gibbs free energy (\(\Delta G\)) of a binary mixture is calculated at 298.15 K [10].

\[
\Delta G = G_{[Na^+(\text{EC})_n(\text{PC})]} - G_{[Na^+EC_{(n-1)}\text{PC}]} - G_{EC} \tag{2}
\]
3. Result and Discussion

Geometry optimization of structures for the study of the interaction of sodium cation with an organic electrolyte comprising EC: PC binary mixture in three different ratios was carried out at the theoretical level of B3LYP/6-31G (d, p). The optimized structures of nEC-PC-Na⁺ (with n=1, 2, 3) complexes are presented in Figure 2. The favorable site for the interaction of Na⁺ ion with carbonate esters is with oxygen atom of C=O as shown in Figure 2. The results are in line with molecular dynamics simulation results, recently reported by Pham et al. [6]. In Table 1 the values of Na⁺-O bond length, Mulliken charge on sodium cation, Mulliken charge on carbonyl oxygen and dipole moment of the mixture is presented. From these values, Na⁺ interaction with the binary mixture of EC and PC can be well understood. In these complexes the distance between Na⁺ and carbonyl oxygen is dependent on the number of carbonate solvents surrounding the Na⁺ ion. As shown in Fig. 2(a),2(b) and 2(c), the average O-Na (ethylene carbonates’ oxygen and sodium cation) bond length in EC-PC-Na⁺, 2EC-PC-Na⁺, 3EC-PC-Na⁺ are 2.290 Å, 2.305 Å and 2.356 Å respectively. The average O-Na (propylene carbonates’ oxygen and sodium cation) bond length in EC-PC-Na⁺, 2EC-PC-Na⁺, 3EC-PC-Na⁺ are 2.256, 2.307 and 2.372 respectively. The stretching of O-Na⁺ bond length is observed with the enlargement of the solvation complexes, implying that solvent molecules are present around the Na⁺ cation in the inner solvation shell structure [12]. From Table 1, the magnitude of Mulliken charge on sodium ion and the carbonyl oxygen of EC and PC evidences the formation of the cluster and also suggest that sodium ion is compatible with different compositions of carbonates [6]. The results in Table 1 infer better stability of 3EC-PC-Na⁺ in comparison to other ratios of a binary mixture on the basis of dipole moment.

**Table 1:** Distance between Na⁺ and O (carbonyl oxygen atom), charge on Na⁺, Mulliken charge on O (in C=O group of EC and PC) and dipole moment of its mixtures.

| Binary Mixtures | Distance between Na⁺ and O (EC, PC), d_{Na⁺-O} | Mulliken Charge on Na⁺ (|e|) | Mulliken Charge on O (|e|) | Dipole moment D(Debye) |
|-----------------|-----------------------------------------------|----------------------------|----------------------------|------------------------|
| 1:1:1           | 2.290, 2.256                                 | 0.116                      | -0.493, -0.505              | 4.37                   |
| 2:1:1           | 2.305, 2.307                                 | 0.277                      | -0.477, -0.483              | 4.50                   |
| 3:1:1           | 2.356, 2.372                                 | 0.440                      | -0.519, -0.533              | 4.82                   |
Table 2. Binding energy $\Delta E$ (in Kcal/mol) and Gibbs free energy $\Delta G$ (in Kcal/mol) of binary mixtures.

| Reactions | $\Delta E$ | $\Delta G$ |
|-----------|------------|------------|
| $Na^+ + (EC)_1 + PC \rightarrow Na^+(EC)_1PC$ | -150.61 | -66.49 |
| $Na^+ + (EC)_1PC + EC \rightarrow Na^+(EC)_2PC$ | -175.71 | -68.82 |
| $Na^+ + (EC)_2PC + EC \rightarrow Na^+(EC)_3PC$ | -194.53 | -78.44 |

The values of binding energy ($\Delta E$) are presented in Table 2. The values indicate the dependence of binding energy on the number of carbonate molecule coordinated to Na$^+$ ion. The binding energy increases as the concentration of EC is increased. Among the EC-PC-Na$^+$ clusters; 3EC-PC-Na$^+$ exhibits the highest binding energy (BE). Generally, the high solubility of salts in solvents is required while designing a new electrolyte [14]. “The basic hypothesis is that for a successful ion-solvent system the ion should have favorable free energy of solvation in a particular solvent” [1]. The stepwise Na$^+$ solvation reactions Gibbs free energy values in nEC-PC-Na$^+$ (1 ≤ n ≤ 3), with the change of solvent numbers are reported in Table 2. The negative value of Gibbs free energy of solvation ($\Delta G$) in all the complexes indicates that Na$^+$ solvation in the considered ratios of EC:PC will proceed favorably. The result demonstrates that with the increase in the concentration of EC in nEC-PC-Na$^+$ (1 ≤ n ≤ 3), Gibbs free energy of solvation ($\Delta G$) increases. The maximum Gibbs free energy value is seen for 3EC-PC-Na$^+$ complex, indicating (3:1) ratio of EC:PC as an optimal composition than other ratios of binary mixtures of carbonates; for it to be used as electrolyte in sodium-ion batteries.

Figure 2: Optimized structure of a) EC-PC-Na$^+$, b) 2EC-PC-Na$^+$, & c) 3EC-PC-Na$^+$ complexes and IR Spectra for d) EC-PC-Na$^+$, e) 2EC-PC-Na$^+$, & f) 3EC-PC-Na$^+$ complexes.

Infrared spectra analysis in the spectral range of 400 to 3200 cm$^{-1}$ provides further understanding of the interaction of Na$^+$ cation and carbonates [9]. Table 3 lists the calculated infrared (IR)
frequencies of specific modes of vibrations of nEC-PC-Na⁺ (1 ≤ n ≤ 3) complex. The theoretical IR spectra of EC-PC-Na⁺, 2EC-PC-Na⁺ and 3EC-PC-Na⁺ is displayed in Figure 2(d), 2(e) and 2(f) respectively. The stronger peak between 1875.89-1894.99 cm⁻¹ corresponding to C=O bond stretching vibration. It moves to a higher frequency with the increasing percentage of EC in the complexes of nEC-PC-Na⁺ (1 ≤ n ≤ 3).

**Table 3.** Calculated IR frequency (cm⁻¹) at particular modes of vibrations for EC and Na⁺-EC complex in the gas phase.

| Modes (ν) | EC-PC-Na⁺ | 2EC-PC-Na⁺ | 3EC-PC-Na⁺ | Assignment               |
|----------|-----------|------------|------------|-------------------------|
| ν₁       | 1884.48   | 1890.69    | 1894.19    | C=O stretching          |
| ν₂       | 1552.48   | 1549.59    | 1548.43    | CH₂ twisting            |
| ν₃       | 1216.65   | 1113.09    | 1108.34    | C-O stretching          |
| ν₄       | 1098.01   | 1081.55    | 1053.45    | Ring stretching         |
| ν₅       | 298.43    | 185.88     | 182.58     | Na⁺-O stretching        |

Besides, the vibrational frequency of little peak between 1518.40 to 1552.58 cm⁻¹ and stronger peak between 1100.86 to 1216.65 cm⁻¹ corresponds to twisting of CH₂ and stretching of C-O of different carbonates. The vibration peak between 1050.32-1098.55 cm⁻¹ is ascribed to stretching of EC ring in of nEC-PC-Na⁺ (1 ≤ n ≤ 3) complexes. Shifting in the aforementioned peaks to lower frequency direction is observed with the decrease in the concentration of Na⁺ ion in the solvation complex from EC-PC-Na⁺ to 3EC-PC-Na⁺. As reported in Table 3, the vibration peak for the mode ν₃ represents stretching of O-Na in nEC-PC-Na⁺ (1 ≤ n ≤ 3) complexes, which shifts to lower frequency with the increase in number of EC molecule from EC-PC-Na⁺ to 3EC-PC-Na⁺. The stability of EC-PC-Na⁺ electrolyte system and its higher EC content conjugates is assured by such changes in the active infrared modes. These changes are the result strong cation-solvent interaction [15].

**4. Conclusion**

The paper deals with the DFT studies on interaction of sodium ion with commonly used electrolytes EC and PC. In this paper, emphasis has been given to calculate the interaction energy of sodium ion with electrolytes and also to calculate the IR spectra of complexes. DFT study was performed on the different composition of binary mixture EC and PC, that are very useful organic solvents. To explore the Na⁺ solvation in carbonate ester solvents the structural and electronic properties of EC-PC-Na⁺ complex in three different ratios of EC:PC is compared. The stepwise solvation was found to be very spontaneous implying that the cyclic carbonate ester can easily solvate Na⁺ ion. Through the theoretical spectra output, it is well demonstrated that the vibration ascribed to the stretching of C=O bond and C-O bond in carbonate esters shifts towards higher and lower frequency respectively with increasing percentage of EC in EC-PC-Na⁺. Moreover, in the DFT calculation performed salt anions have not been taken into consideration. To deeply understand the solvation mechanism of electrolyte, an extensive amount of research is still needed to be done by combining different salts, solvents and additives that would guide for assessing the feasibility of electrolyte for application in sodium-ion batteries.

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