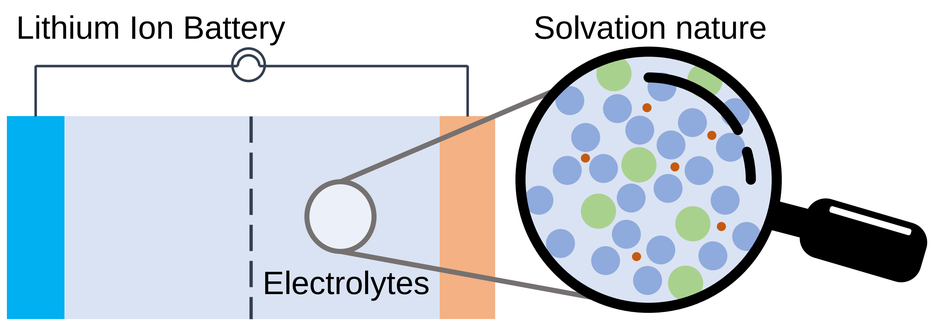
Solvation Structure study of Lithium-Ion Battery Electrolytes by FTIR and PFG-NMR spectroscopy

Chaiho Lim[1,2], Joo Hyun Kim[2], Kyung-koo Lee[3]*, Kyungwon Kwak[1,2]*, Minhaeng Cho[1,2]*

[1] Center of Molecular Spectroscopy and Dynamics, Institute for Basic Science(IBS)
[2] Department of Chemistry, Korea University
[3] Department of Chemistry, Kunsan National University

Introduction



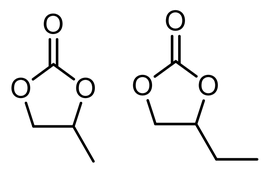
Lithium ion batteries are relevant to a wide range of portable electronic device due to high charge density of lithium ion among other materials. The performance of lithium ion in the lithium ion batteries depends on the choice of the medium for lithium ion electrolytes. Electrolytes play a key role in ion dissociation and diffusion of lithium salt from cathode to anode in the lithium ion battery. Usually, lithium ion electrolytes are based on solution consisting of cyclic carbonates and linear carbonates such as propylene carbonate (PC) and dimethyl carbonate (DMC) respectively. It is important to study molecular detail such as solvation structure and dynamics for understanding lithium ion electrolyte properties. In this study, solvation number and ion association rate of LIB electrolytes was determined by FTIR spectroscopy and PFG-NMR spectroscopy, respectively.

Solvation Structure

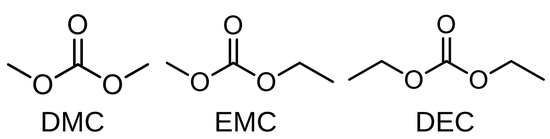
Samples

Solvent

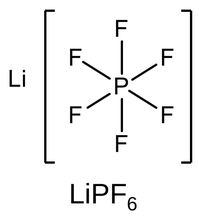
Cyclic Carbonate



Linear Carbonate

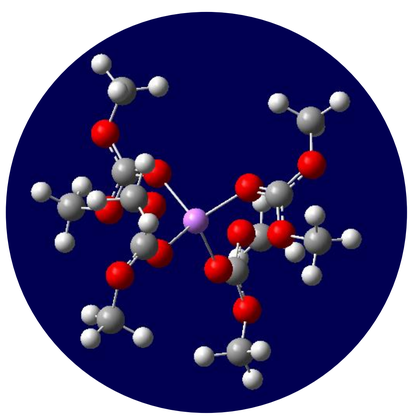


Salt

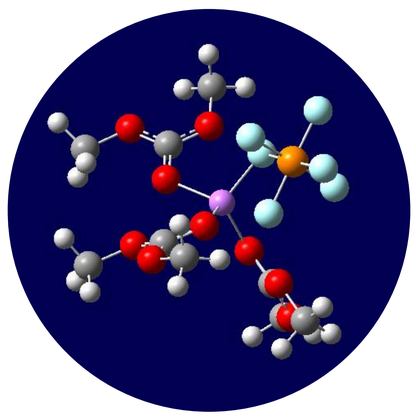


Ion Association

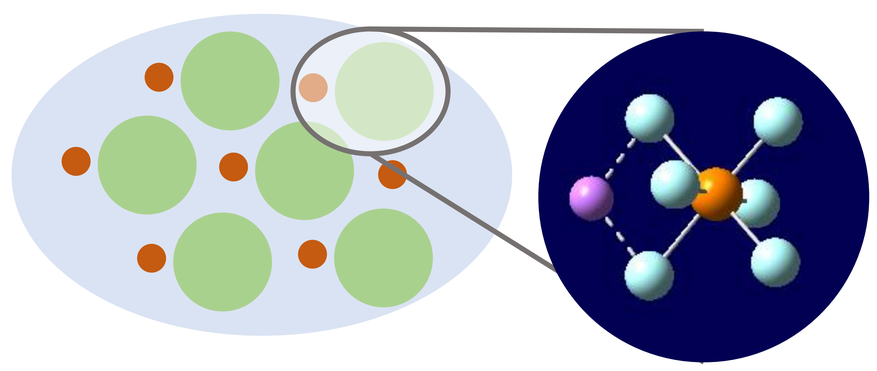
Free Ion



Contact Ion Pair (CIP)

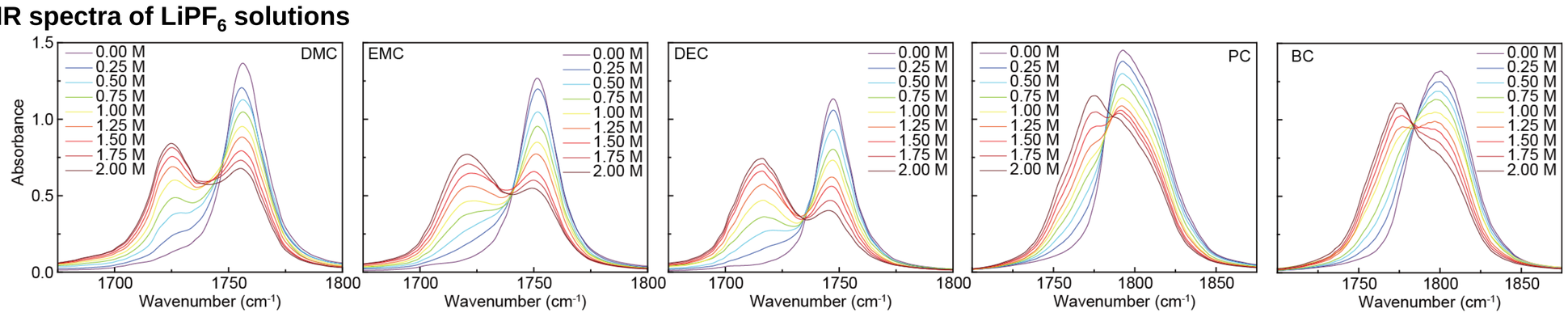


Agglomerate (AGG)



Solvation Number

FTIR spectra of $LiPF_6$ solutions



Area plot of free vs bind complex

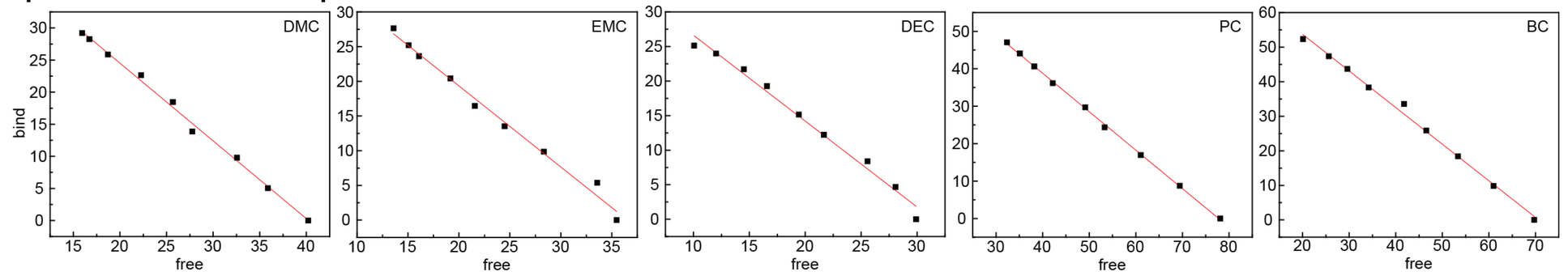


Table 1. The square of the transition dipole moment ratio

	Experiment	DFT Calculation
DMC	1.21	1.19
EMC	1.16	1.19
DEC	1.24	
PC	1.03	1.09
BC	1.05	1.10

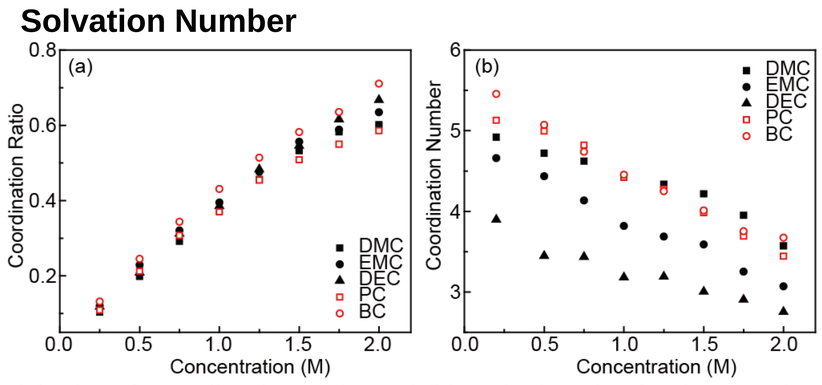
$$A_f + A_b = \left(1 - \frac{\mu_b^2}{\mu_f^2}\right) A_f + C_{total}\mu_b^2$$

$$A_b = -\frac{\mu_b^2}{\mu_f^2} A_f + C_{total}\mu_b^2$$

$$\text{Solvation Number} = \frac{C_b}{C_b + C_f} \times \frac{C_{total}}{C_{lithium}}$$

$$\text{SolvationNumber} = \frac{A_b}{A_b + \left(\frac{\mu_b^2}{\mu_f^2}\right) A_f} \times \frac{C_{total}}{C_{lithium}}$$

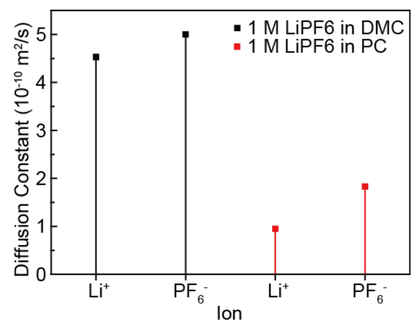
Solvation Number



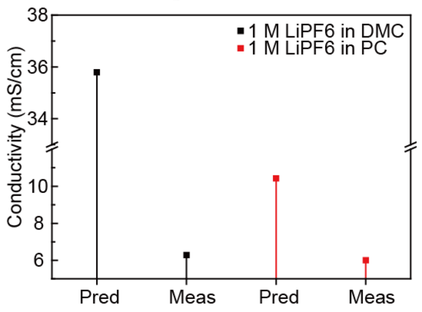
(a) Plot of coordination ratio and (b) Calculated solvation number of DMC, EMC, DEC, PC and BC at various $LiPF_6$ concentrations.

Ion Association

Diffusion Constant

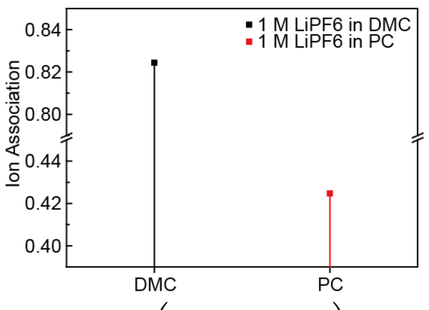


Conductivity



$$\sigma_{\text{Predicted}} = \frac{Nq^2}{k_B T}[D^+ + D^-]$$

Ion Association



$$\alpha = \left(1 - \frac{\sigma_{\text{measured}}}{\sigma_{\text{Predicted}}}\right)$$

Conclusion

We studied solvation structure and ion association rate of organic carbonate based lithium-ion battery electrolytes by FTIR spectroscopy and PFG-NMR spectroscopy. Solvation number of lithium ion was estimated by area ratio of free and bind peak of FTIR spectra. To correct the effect of the transition dipole moment, we obtained the ratio of square of transition dipole moment by linear fit between area of free and bind complex. Solvation number of lithium ion had inverse relation between concentrations. Decrease of solvation number of lithium ion with increasing concentration is related to formation of ion association. Solvation number of cyclic carbonates had similar quantity, but solvation number of linear carbonates decreased with increasing methyl group. The amount of ion association was studied by PFG-NMR spectroscopy and conductivity measurement. The amount of ion association was estimated using Nernst-Einstein equation. The result showed that large amount of lithium ions was in ion association state. The ion association rate of DMC was about two times higher than that of PC.