# Characterization of organic electrolyte systems by nuclear magnetic resonance and molecular orbital simulation: equilibrium constant and net charge distribution in solvation state

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## Abstract

Solvation states of single solvent electrolyte systems of ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ehylmethyl carbonate (EMC) and diethyl carbonate (DEC) with $LiPF_6$ were characterized by $^{13}C$-NMR solvation shift and molecular orbital (MO) simulation. Dissociation constants and solvation constants were estimated by parameter fitting to solvation shift using a simple equilibrium model. The solvation shifts $\Delta\delta$ were observed not only at a lower field but also at a higher field due to change of net charge $\Delta\rho$ in solvent molecules by $Li^+$ attachment. This particular feature of solvation shifts was demonstrated in the molecular orbital simulation as driven by the change of net charge using a 1:1 ($Li^+$:solvent) solvation model. © 1997 Elsevier Science S.A.

*Keywords:* Organic electrolytes; Solvation; Nuclear magnetic resonance. Equilibrium constant; Molecular orbital simulation; Net charge

## 1. Introduction

The organic solvent chosen determines the physical properties of the electrolyte and cell performance of a lithium-ion secondary battery. However, the choice of the electrolyte is still a trial-and-error process because even solvents having a similar chemical structure show a different behavior. To design an electrolyte by molecular simulation, it is necessary to correlate the physical properties of the electrolyte with the chemical structures of solvent and anion. Recently, molecular orbital (MO) simulations have been applied to elucidate the solvation structure [1]. This work aims at understanding the solvation states of cyclic and linear carbonate compounds in a single solvent electrolyte system.
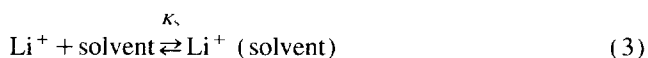
## 2. Experimental

Commercially available organic solvents, ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC) and diethyl carbonate (DEC) and $LiPF_6$ were used. The 0.5, 1.0 and 2.0 M single solvent electrolytes were prepared in an argon-filled

glove box. $^{13}C$-NMR chemical shifts of organic solvents and electrolyte were recorded on a JEOL JNM-GX400 FT-NMR with an external standard of tetramethylsilane (TMS) at 25 °C, except for EC which was recorded at 40 °C.

Solvation shifts ($\Delta\delta$) were estimated by Eq. (1), where $\delta_s$ and $\delta_0$ represent chemical shifts of electrolyte (with salt) and solvent (without salt), respectively

$$\Delta\delta = \delta_s - \delta_0 \tag{1}$$

$\Delta\delta$ is a function of the molar ratio ($\tau$) of $LiPF_6$ to the solvent and is denoted $\Delta\delta(\tau)$. Because the chemical shifts of electrolyte are observed as an average of free solvent and solvated solvent, the critical solvation shift $\Delta\delta'$ (the net shift for solvated molecule) must be estimated by analyzing the experimental $\Delta\delta(\tau)$. Using the simplest equilibrium process written in Eqs. (2) and (3), the equilibrium constants of $K_d$ (dissociation constant, inverse of association constant $K_a$), $K_s$ (solvation constant) and $\Delta\delta'$ were estimated by parameter fitting to the experimental $\Delta\delta(\tau)$ [2]

$$LiPF_6 \overset{K_d}{\rightleftarrows} Li^+ + PF_6^- \tag{2}$$

$$Li^+ + solvent \overset{K_s}{\rightleftarrows} Li^+ (solvent) \tag{3}$$

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## 3. Computational method

Molecular orbital calculations were performed with the MOPAC version 94.1 program on an IBM workstation associated with CAChe® software. A 1:1 (Li$^+$:solvent) solvation structure model binding with carbonyl oxygen was optimized with and without the COSMO (conductor-like screening model) method [3]. Change of net charges on the solvent molecule ($\Delta\rho$) was estimated by comparing the calculation results for a solvent molecule in the neutral state ($\rho_0$) and the solvation state ($\rho_s$), as expressed by Eq. (4). The solvation enthalpy $\Delta H$ was calculated by Eq. (5), where $H_s$ is the heat of formation for the solvation state, $H_0$ is that for the neutral state and $H_{Li}$ is that for Li$^+$.

$$\Delta\rho = \rho_s - \rho_0 \qquad (4)$$

$$\Delta H = H_s - (H_0 + H_{Li}) \qquad (5)$$

## 4. Results and discussion

Fig. 1 shows the solvation shift $\Delta\delta$ as a function of the molar ratio, $\tau$, along with the calculated curve determined by parameter fitting for the PC electrolyte system. As shown in this figure, the solvation to Li$^+$ caused not only a lower field shift (charge reduction), but also a higher field shift.

Table 1 summarizes $K_d$, $K_s$ and critical solvation shift for $\Delta\delta'$ each carbon atom of the solvent molecules. Higher values of $K_d$ and $K_s$ for EC may be due to the higher observation temperature (40 °C). $K_d$ and $K_s$ for EMC were highest among linear carbonate compounds, suggesting a steric effect due to an asymmetric structure. $K_d$ and $K_s$ for DEC were lower, this must be due to its large alkyl group. $>$C=O had a larger $\Delta\delta'$
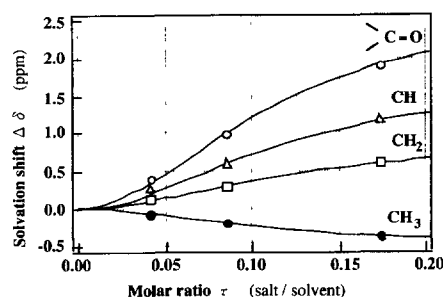


Fig. 1. Solvation shift as a function of salt to solvent molar ratio for PC electrolyte system. The calculated curves are drawn with $K_d$, $K_s$ and the critical shift determined by parameter fitting.

in the cyclic carbonate compounds, while CH$_2$ carbon showed a larger $\Delta\delta'$ in the linear carbonate compounds. $\Delta\delta'$ of carbon beside –O– must be large in the case of solvation using –O– oxygen. This suggests that $>$C=O oxygen bonding was dominant in cyclic carbonate compounds, while –O– oxygen bonding may take place in linear carbonate ones.

Table 2 lists enthalpies $\Delta H(\epsilon)$ calculated with the COSMO method using the dielectric constant of the pure solvent, enthalpies calculated in vacuum $\Delta H(1)$ and $\Delta\rho(\epsilon)$ and $\Delta\rho(1)$ using the $>$C=O bonding 1:1 solvation model. $\Delta\rho(1)$ could explain the sign of $\Delta\delta'$ but not in good order. Thus, the sign change of $\Delta\delta'$ was due to charge alternation of solvent molecule caused by bonding to Li$^+$ as illustrated in Fig. 2. $\Delta\rho(1)$ for $>$C=O was much larger than those for CH$_3$ and CH$_2$. While $\Delta\rho(\epsilon)$ did not give negative values for the CH$_3$ group in PC and DEC, it gave no positive values for $>$C=O carbon in PC and EC. There are two ways to explain these results: (i) $\epsilon$ of the electrolyte solution is not the same as pure solvent, and (ii) the solvation model is unsuitable. Fig. 3 shows the variation of change of net charge $\Delta\rho(\epsilon)$ as a function of $\epsilon$ for $>$C=O and CH$_3$ of PC. As $\epsilon$ increased,

Table 1

Equilibrium constants, $K_d$, $K_s$ and critical solvation shifts $\Delta\delta'$

| Solvent | $K_d$ (mol) | $K_s$ (mol) | $\Delta\delta'$ (ppm) $>$C=O | CH$_2$ | CH$_3$ | (O)CH$_3$ | CH |
|---------|------|------|------|------|------|------|------|
| EC | 213 | 1138 | 0 9 | 0.3 | | | |
| PC | 56 | 107 | 2 6 | 0.8 | −0.5 | | 1 6 |
| DMC | 85 | 250 | 1 1 | | | 1.0 | |
| EMC | 135 | 203 | 1.1 | 1 6 | −0.2 | 1.2 | |
| DEC | 81 | 61 | 1 6 | 2 2 | −0 6 | | |

Table 2

Calculated enthalpy and change of net charge in vacuum ($\epsilon = 1$) and in dielectric medium ($\epsilon$ of each solvent)

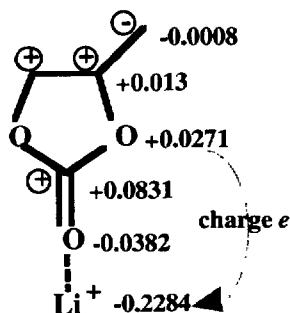| Solvent | $\epsilon$ | Enthalpy (kJ mol$^{-1}$) | | $\Delta H(\epsilon)$-left/$\Delta\rho(1)$-right ($10^{-2}$) | | | | |
|---------|-----|------|------|------|------|------|------|------|
| | | $\Delta H(\epsilon)$ | $\Delta H(1)$ | $>$C=O | CH$_2$ | CH$_3$ | (O)CH$_3$ | CH |
| EC | 89 | −363 | −138 | −0.5/8.1 | 0.7/0.7 | | | |
| PC | 65 | −360 | −142 | −0 6/8 3 | 0 9/0.1 | 0.5/−0.8 | | 0.4/1.3 |
| DMC | 3 1 | −303 | −126 | 3.4/2 1 | | | 1.1/1.7 | |
| EMC | 2.9 | −301 | −129 | 3 7/7.4 | 1 5/1.8 | −0.2/−1 0 | 1.1/4.0 | |
| DEC | 2.8 | −303 | −141 | 2.6/7.4 | 1.4/8.0 | 0 0/−2.9 | | |

Fig. 2 Illustration of solvation shift direction and change of net charge, $\Delta \rho$ (in vacuum $\epsilon = 1$), for PC: ($\oplus$) low field shift, and ($\ominus$) high field shift
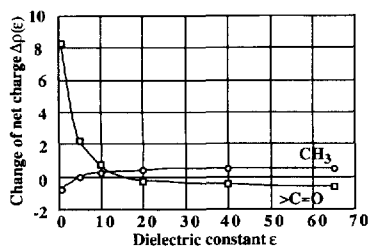


Fig. 3. Change of net charge $\Delta \rho(\epsilon)$ vs. dielectric constant $\epsilon$ for PC.

$\Delta \rho(\epsilon)$ for $>C=O$ decreased and $\Delta \rho(\epsilon)$ for $CH_3$ increased. At $\epsilon$ around 3, $\Delta \rho(\epsilon)$ could well explain $\Delta \delta'$. But for linear carbonate compounds, decreasing $\epsilon$ did not lead to a good $\Delta \rho(\epsilon)$ ratio of $>C=O$ to $CH_2$, this ratio was much bigger than its $\Delta \delta'$ ratio. For cyclic carbonate compounds, the $>C=O$ oxygen bonding solvation model and lowering $\epsilon$ are

suggested. For linear carbonate compounds, another solvation model is needed to explain the $\Delta \delta'$ by $\Delta \rho$. By considering these factors, $\Delta H(\epsilon)$ may show better correlation with $K_s$ (it must be related to $\Delta G = -RT \ln K$, if $\Delta S$ is not large), and further simulation is needed in this sense.

## 5. Conclusions

Characterization of a pure solvent electrolyte system of cyclic and linear carbonate compounds by NMR solvation shifts and MO simulation suggested that cyclic compounds solvated to $Li^+$ with $>C=O$ oxygen and the dielectric constants of their electrolyte may be smaller than those of pure solvents, while linear carbonates may not only bond to $Li^+$ with $>C=O$ oxygen but also $-O-$ oxygen. MO simulation derived a net charge deviation in the solvent molecule by $Li^+$ solvation. This explained the higher field solvation shift of certain atoms in solvent molecules even in the case of bonding to $Li^+$ cation.

## References

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