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Dielectric Properties of Ethylene Carbonate and Propylene Carbonate using Molecular Dynamics Simulations

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Ethylene carbonate (EC) and propylene carbonate (PC) are two widely used solvents in Li-ion batteries and super-capacitors. Ion diffusion in these solvents depends strongly on accurate predictions of solvent dielectric properties. We used all-atom molecular dynamics simulations of these pure solvents to calculate dielectric constants and dielectric relaxation times at various temperatures. The dielectric constant measures polarization of a material whereas dielectric relaxation measures the lag of the polarization in a dielectric medium in responding to a change in an applied field. Predicted values are compared with the available experimental results to validate the force field parameters (OPLS-AA) for these solvents. Current results for dielectric constant and dielectric relaxation times indicate that OPLS-AA force field produces reasonable agreement with experiment for both EC and PC.

Introduction

Ethylene carbonate (EC) and propylene carbonate (PC) are widely used cyclic carbonates for battery applications.[1] These cyclic carbonates have high dielectric constant required for efficient transport of lithium ions but its limited by high viscosity of these electrolytes. These electrolytes are often used with other low viscosity materials to achieve fast ion transport.[1] Experimental and simulations studies on dielectric properties of these pure solvents at wide range of temperatures are limited.[2–6] In this transaction, we address the dielectric constant and dielectric relaxation times for the pure EC and PC electrolytes at wide range of temperatures. Molecular simulation studies with all atom force field will be carried out and compared against available experimental results.

Dipole relaxation processes of EC and PC has been investigated in order to better understand its dynamical properties. Dielectric relaxation accesses the lag of the polarization of a material in responding to a change in an applied electric field. The molecular polarization in a dielectric medium does not respond to a changing electric field instantly. This delay is dependent on the frequency of a changing electric field. At low enough frequency, dielectric constant keep the same because the orientation of the dipoles can still keep up with the changing field. With increase of frequency, the dipoles start to lag behind the field.[7] The frequency dependent dielectric constant can be written as,[7–9]

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega). \qquad (1)$$

The imaginary part $\epsilon''(\omega)$ is referred to dielectric loss, represents the loss of energy which is converted to heat. The relationship between $\epsilon(\omega)$ and the Fourier transform of the dipole

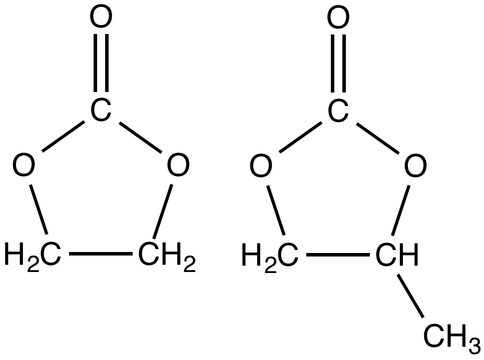

FIG. 1: Chemical structures of ethylene carbonate (EC) and propylene carbonate (PC).

moment autocorrelation function $P(t)$ is given by,[2,9,10]

$$\frac{\epsilon'(\omega) - i\epsilon''(\omega)}{\epsilon_r - \epsilon_\infty} = 1 - i\omega \int_0^\infty P(t)\mathrm{exp}(-i\omega t)\mathrm{d}t, \tag{2}$$

with $\epsilon_r = \epsilon/\epsilon_0$ the static dielectric constant (Fig. 2(a)), $\epsilon_\infty = 1$ in the absence of electronic polarization in the system and

$$P(t) = \frac{\langle M(0)M(t)\rangle - \langle M(0)\rangle^2}{\langle M(0)^2\rangle - \langle M(0)\rangle^2}, \tag{3}$$

$M(t)$ is the dipole moment of the simulation system at time t.

The computed $P(t)$ was fitted to a Kohlrausch-Williams-Watts (KWW) model,

$$P_{\mathrm{KWW}}(t) = \mathrm{exp}[-(t/\tau)^\beta]. \tag{4}$$

The fitted results was used in eq 2 to obtain the real and imaginary part of frequency dependent dielectric constant.[10] The temperature dependence of relaxation time may be modeled as,

$$\tau = A\mathrm{exp}(\beta\Delta H^*), \tag{5}$$

where the ΔH^* is the molar activation enthalpy. A is the pre-exponential factor, which can be assumed to have a temperature dependence or treated as a constant. However, the exact form of this pre-factor haven't been reached an agreement in the historical studies.[2,11,12]

Excluding the pre-factor A, the relationship between relaxation time the activation enthalpy can be represented as

$$\ln(\tau) \propto \beta\Delta H^*. \tag{6}$$

Therefore, ΔH^* can be evaluated from the slope of linear plot $\ln(\tau) \approx 1/T$ (Fig. 2(b)).

Methods

Molecular dynamics simulations were carried out using Gromacs[13] simulation package. Solvent molecules (EC and PC) were placed randomly in the cubic simulation box to generate initial configurations. OPLS-AA force field[14] parameters were used to represent both

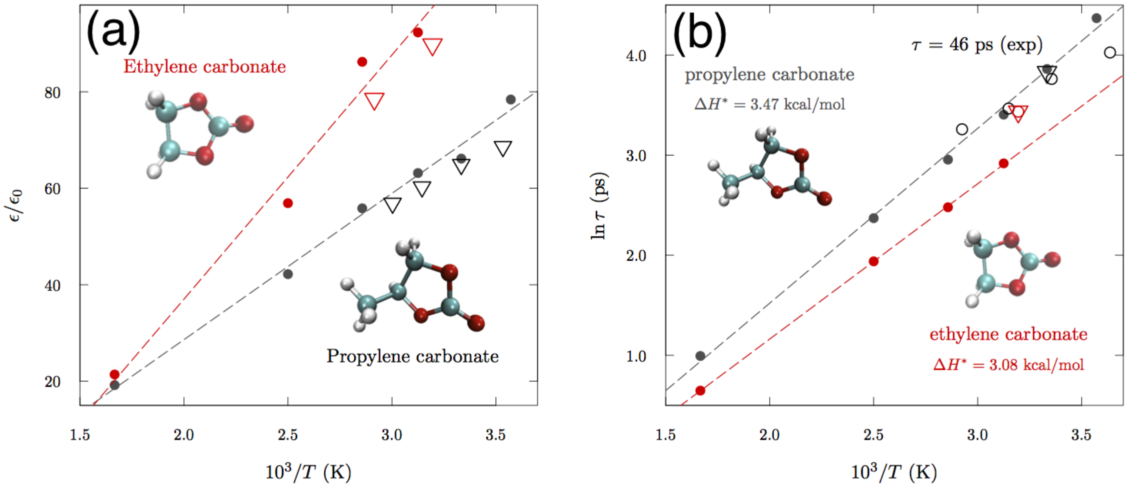

FIG. 2: (a) Static dielectric constant and (b) Dipole relaxation time of EC and PC at various temperatures. Experimental data is shown in open triangles and circles.

EC and PC molecules. The energy minimization and 1 ns of density equilibration step was followed by 50 ns production run using constant pressure ensemble. The configurations were sampled every 0.5 ps and used for dielectric constant calculations. Nosé-Hoover thermostat[15,16] maintained the temperature and Parinello-Rahman barostat[17] was used to keep 1 atm pressure throughout the simulation. Bonds involving hydrogen atoms were constrained using LINCS algorithm.[18] Particle mesh ewald method was used for electrostatic interactions cut-offed at 1.2 nm.

A separate 1 ns simulation was run to calculate dipole autocorrelation function. The configurations were saved at higher frequency (every 0.001 ps) to get a nice smooth auto correlation function. Other simulation conditions were same as before.

Results

The static dielectric constant calculated from the simulation trajectories and corresponding dielectric relaxation times are shown in Table I. At elevated temperature, the molecular random thermal motion is greater, therefore, less perfect alignment with an applied field. This is reflected by reduced static dielectric constant (Fig. 2).

The relaxation time is decreased as temperature increased, which implying the polarization relaxes faster towards a new equilibrium at higher temperature. As a result, the dielectric loss shows a lower and broader peak extending into the higher frequency range. In our temperature range calculated activation enthalpy (ΔH^*) is 3.08 kcal/mol and 3.47 kcal/mol for EC and PC respectively (Fig. 2(b)). The open triangles and circles in Fig. 2 represent experimental values. OPLS-AA force field shown nice agreement with the experimental values for a given temperature range.

	Temp (K)	ϵ/ϵ_0	τ
EC	320	92.3	18.5
	350	86.2	11.9
	400	56.9	7.0
	600	21.4	1.9
PC	280	78.4	78.9
	300	66.2	47.5
	320	63.2	30.1
	350	55.8	19.2
	400	42.2	10.7
	600	19.2	2.7

TABLE I: Static dielectric constant (ϵ/ϵ_0) and relaxation times (τ) of EC and PC at various temperatures.

Conclusion

The OPLS-AA force field parameters for EC and PC provide reasonable agreement with the available experimental data. Static dielectric constant of both the electrolytes decreases with increase in temperature due to increase in thermal motions of molecules. Corresponding relaxation times are also lower at higher temperatures. This study provides a benchmark for force field parameters for EC and PC and can be used to study dielectric properties of mixed electrolytes.

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