



# Broadband and Molecular Dynamics Analysis of Propylene Carbonate and its Binary Mixtures with Alcohols

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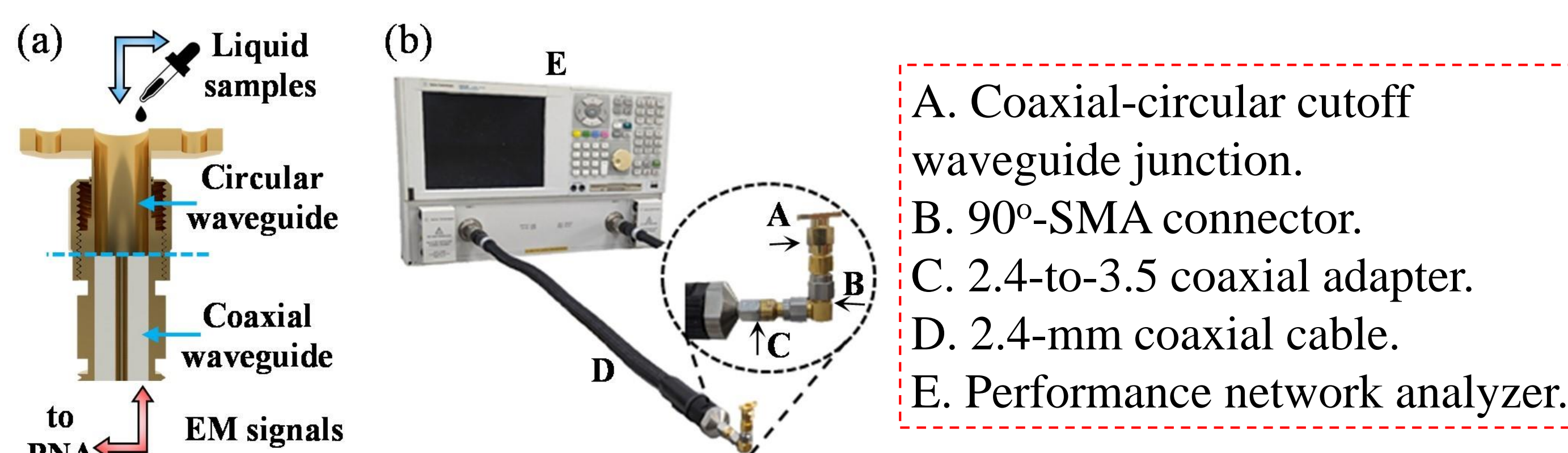
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**Abstract** – This study explores the dielectric properties and relaxation behaviors of propylene carbonate (PC) and its binary blends with methanol and ethanol. Utilizing a coaxial-circular cutoff waveguide junction, broadband dielectric spectra (0.1 GHz to 18 GHz) were characterized, employing a two-group Debye model to extract relaxation parameters. Analysis of excess thermodynamic parameters, Kirkwood orientational correlation factors, and Bruggeman factors for PC-alcohol mixtures was conducted. The data offer insights into microscopic processes, such as the disassociation of alcohol hydrogen-bond networks, formation of new PC-alcohol networks, parallel alignment of dipoles, and enhanced dielectric effects with increasing PC concentration. Molecular dynamics simulations using the TraPPE-UA forcefield exhibited good agreement with experimental results, highlighting the gradual formation of PC-cage and alcohol-cluster microstructures in PC-rich mixtures. These findings hold potential practical applications in high-energy batteries and the pharmaceutical industry.

## I. Introduction

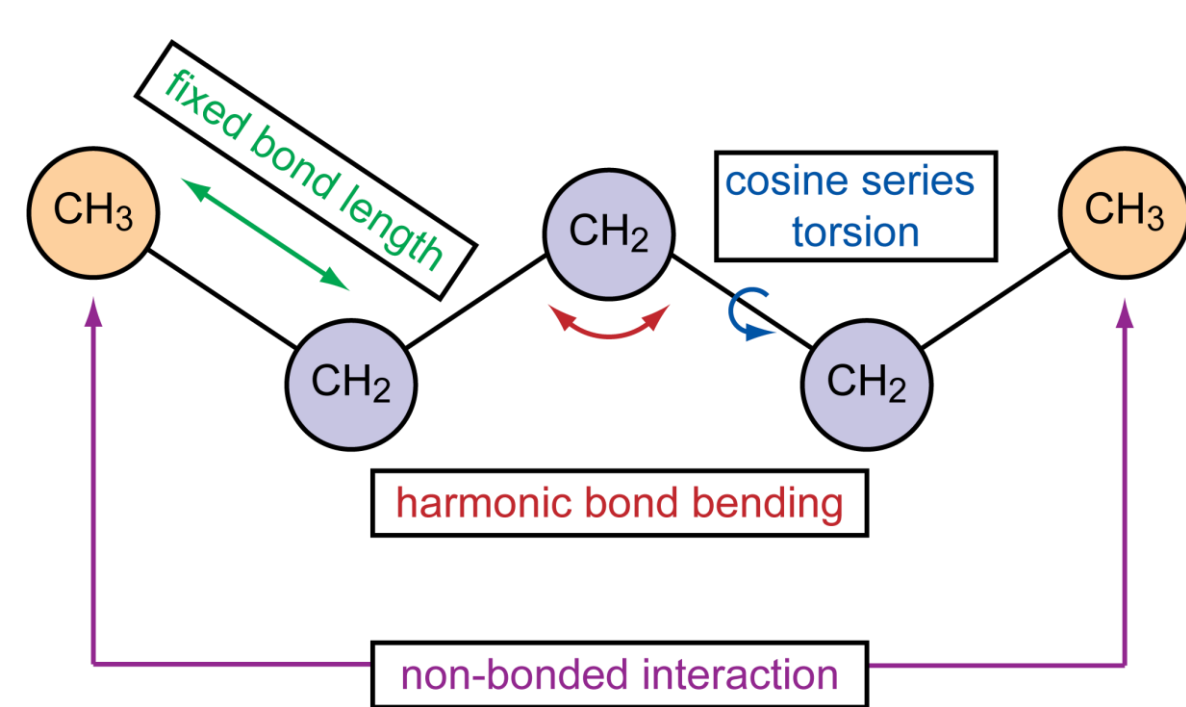
Propylene carbonate (PC) is a standout eco-friendly compound, prized for its water solubility, low toxicity, and biodegradability, making it a preferred choice in various industries such as cosmetics and coatings. Its unique attributes, including substantial static permittivity and compatibility with lithium salts, render PC indispensable in lithium batteries. PC-alcohol mixtures even show great promise as effective solvents in applications ranging from high-energy batteries to pharmaceutical processes. To comprehend these mixtures' dynamics, this study employs broadband dielectric spectroscopy and molecular dynamics simulations, providing insights into changes in H-bond networks and dipole interactions. By characterizing the complex dielectric spectra of PC-methanol and PC-ethanol solvents, the research contributes valuable information, paving the way for innovative applications.

## II. Experimental Setup



**Fig. 1.** (a) The coaxial-circular cutoff waveguide (b) Experimental setup. [1]

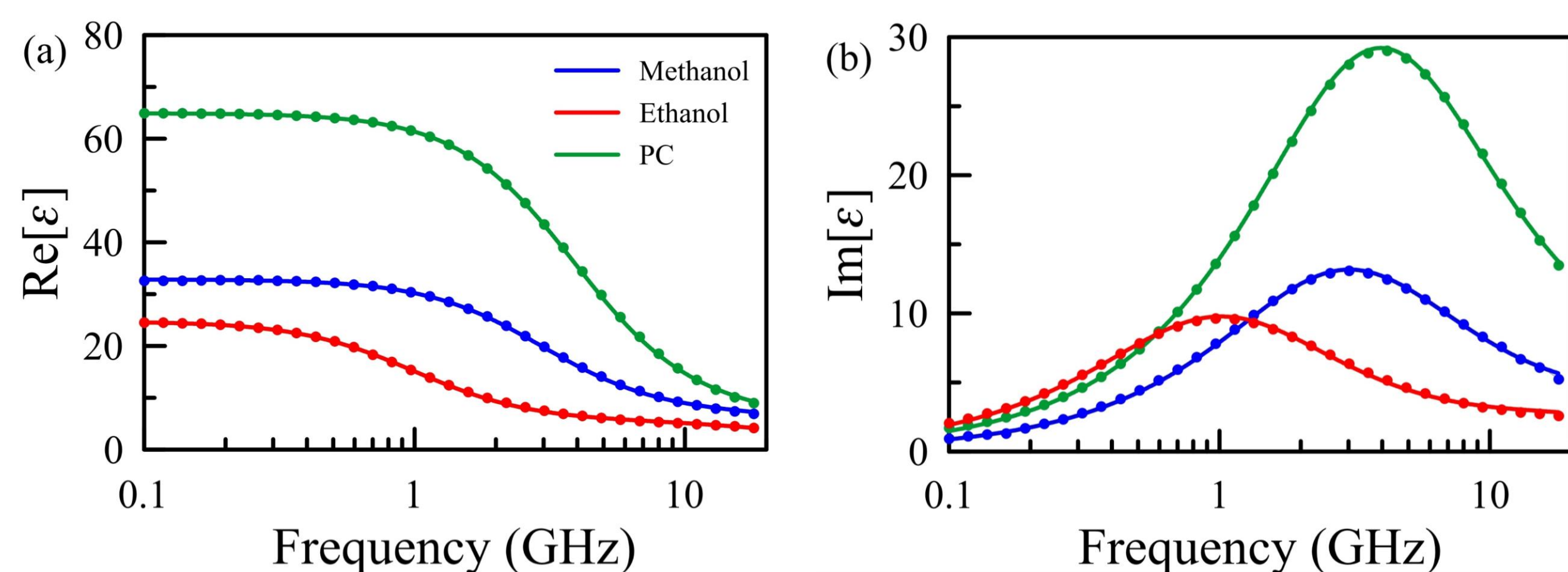
## III. Models and Simulation Details



**Fig. 2.** TraPPE forcefield [2]

- 298K, 1bar
- Unit cell size: 4.6~5.2 nm
- 1000 molecules in total
- Thermostat: v-rescale ( $\tau = 0.1$  ps)
- Barostat: Berendsen ( $\tau = 1.0$  ps)
- Production run: 12 ns; Time step: 1fs

## IV. Pure substances



**Fig. 3.** Dielectric spectra of pure substances

### 2 Debye fitting

$$\epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_1}{1 - i\omega\tau_1} + \frac{\epsilon_1 - \epsilon_\infty}{1 - i\omega\tau_2}$$

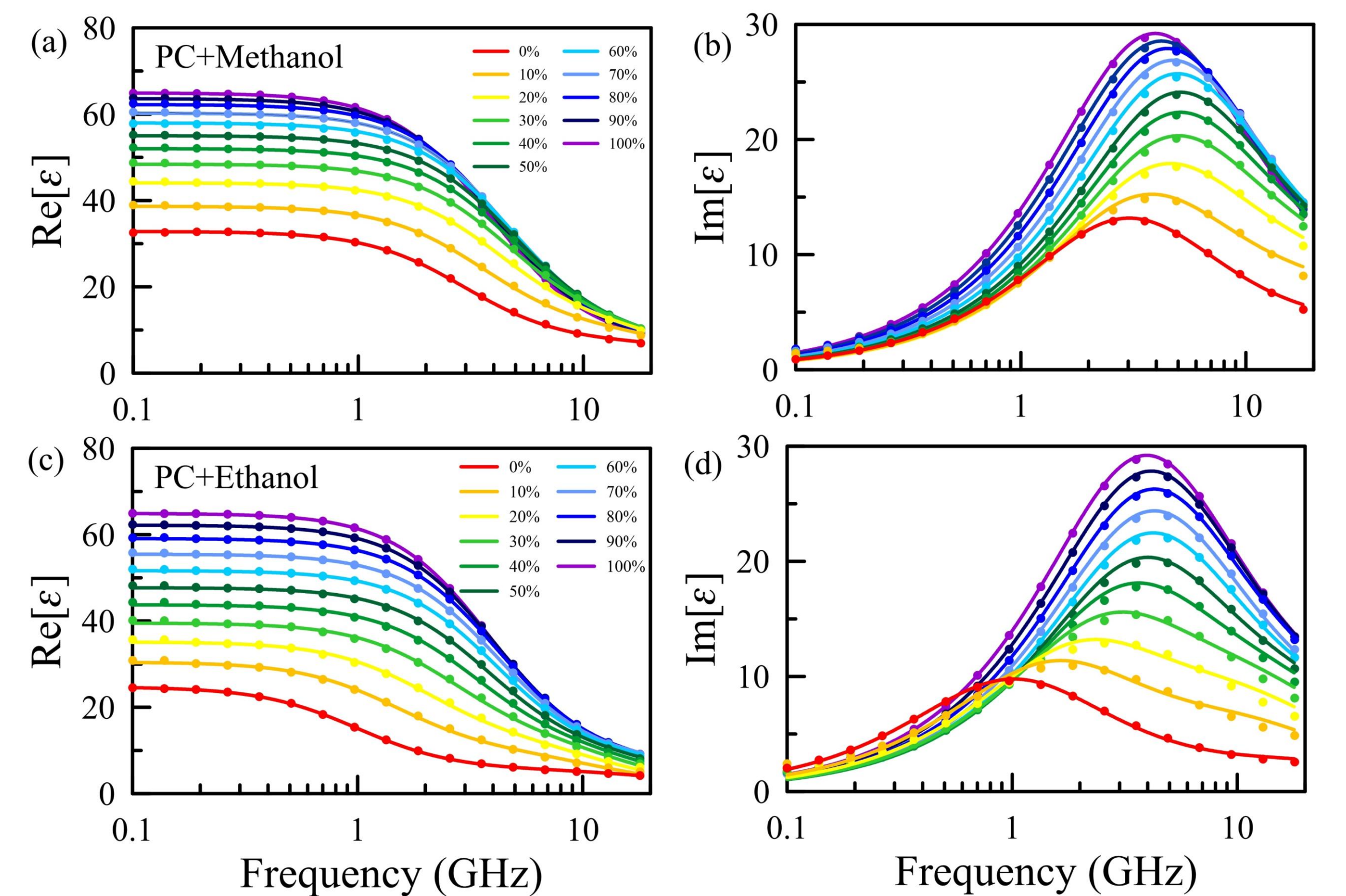
**Table 1.** Relaxation parameters for the three pure substances.

	$\epsilon_s(\epsilon_0)$	$\epsilon_1(\epsilon_0)$	$\epsilon_\infty(\epsilon_0)$	$\tau_1$ (ps)	$\tau_2$ (ps)	$\rho$ (kg/m <sup>3</sup> )	$\mu$ (D)	$g$
PC	64.92	7.41	2.01	40.61	3.44	1205.37	4.90	1.37
MeOH	32.84	7.06	1.76	53.39	2.78	785.83	1.70	3.13
EtOH	24.74	5.51	1.85	158.32	6.89	782.33	1.69	3.21

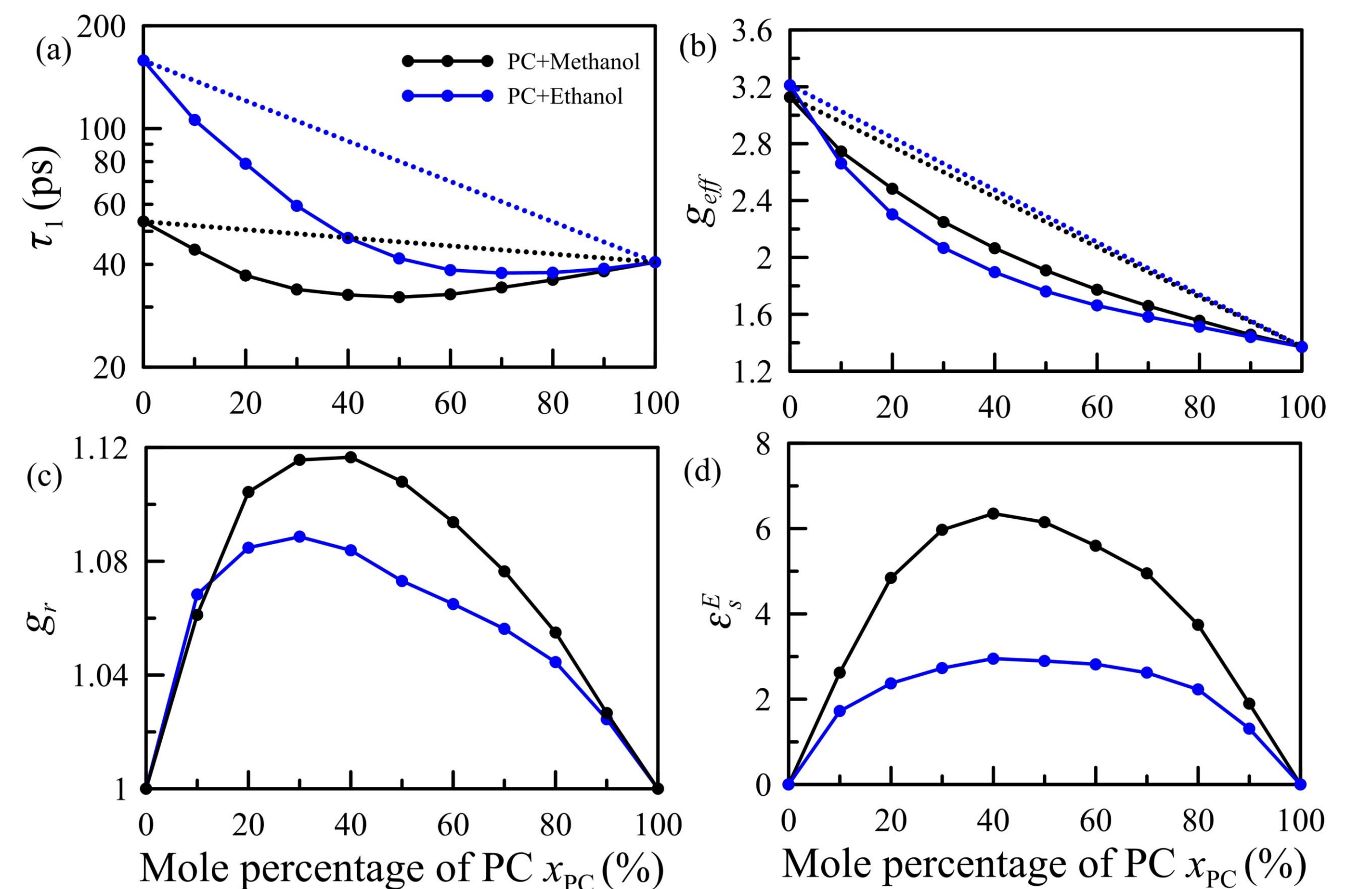
## References

- [1] H.-Y. Yao, Y.-C. Wang, T.-H. Chang, Investigation of dielectric spectrums, relaxation processes, and intermolecular interactions of primary alcohols, carboxylic acids, and their binary mixtures, *J. Mol. Liq.* 353 (2022) 118755.
- [2] J.M. Stubbs, J.J. Potoff, J.I. Siepmann, Transferable Potentials for Phase Equilibria. 6. United-Atom Description for Ethers, Glycols, Ketones, and Aldehydes, *J. Phys. Chem. B* 108 (2004) 17596.
- [3] Z. Luo, S. A. Burrows, S. K. Smoukov, X. Fan, and E. S. Boek, "Extension of the trape force field for battery electrolyte solvents," *The Journal of Physical Chemistry B*, vol. 127, no. 10, pp. 2224–2236, 2023. doi:10.1021/acs.jpcc.2c06993
- [4] B. Chen, J. J. Potoff, and J. I. Siepmann, "Monte Carlo calculations for alcohols and their mixtures with alkanes. transferable potentials for phase equilibria. 5. United-atom description of primary, secondary, and tertiary alcohols," *The Journal of Physical Chemistry B*, vol. 105, no. 15, pp. 3093–3104, 2001. doi:10.1021/jp003882x

## V. Dielectric properties of PC-alcohol mixtures

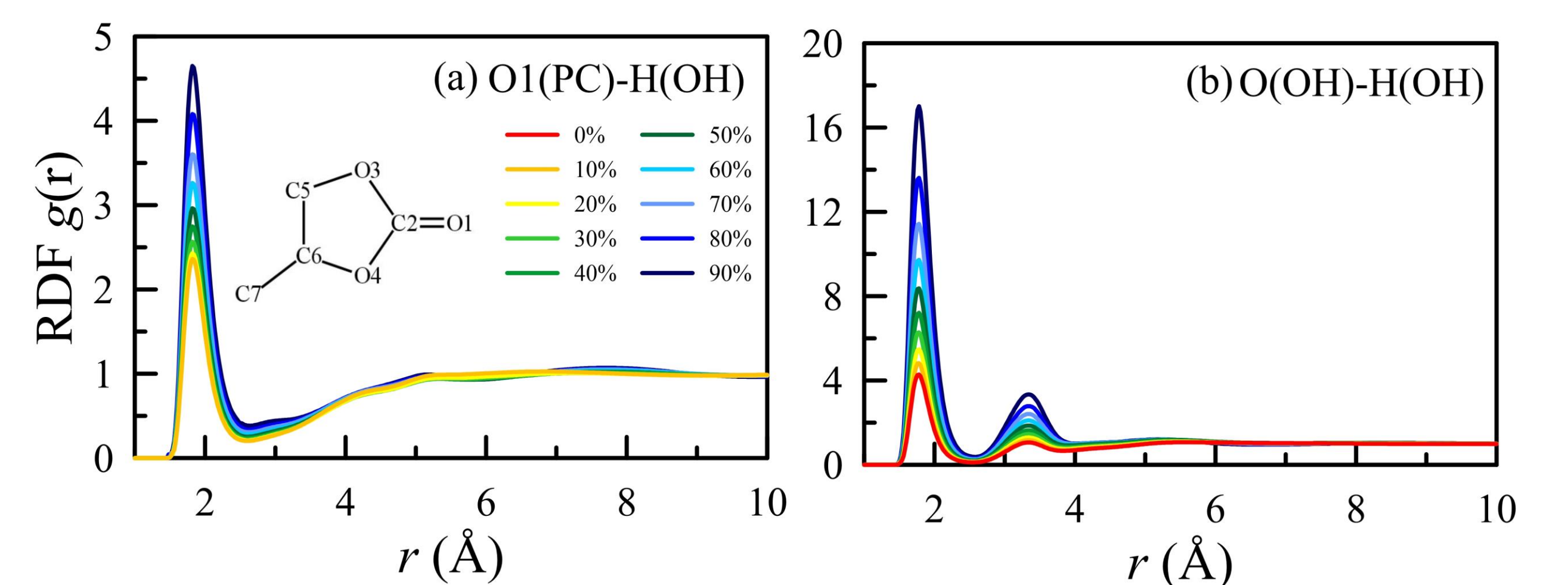


**Fig. 4.** (a)  $\text{Re}[\epsilon]$  and (b)  $\text{Im}[\epsilon]$  of PC-methanol mixtures. (c)  $\text{Re}[\epsilon]$  and (d)  $\text{Im}[\epsilon]$  of PC-ethanol mixtures. Dots represent the experimental data, and solid curves are the fitting results of the 2DB relaxation model.

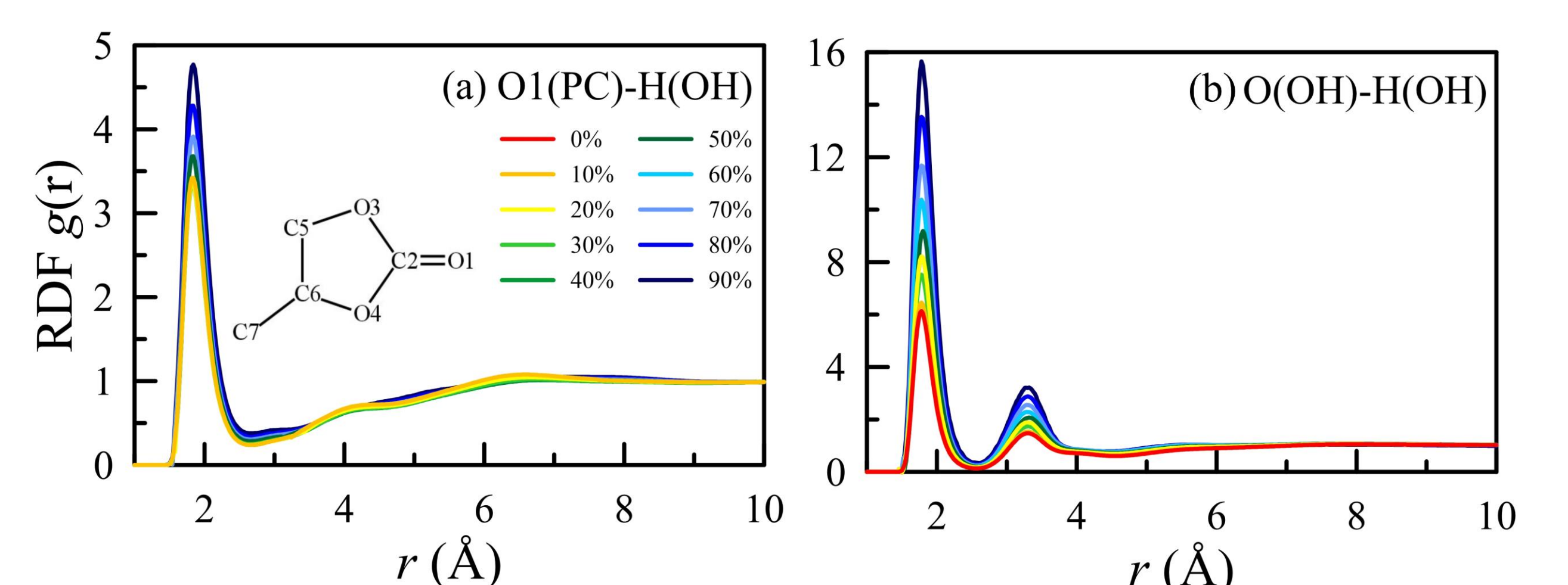


**Fig. 5.** (a) Primary network relaxation time  $\tau_1$ , (b) Effective Kirkwood correlation factors  $g_{eff}$ , (c) Corrective Kirkwood correlation factor  $g_r$ , (d) Excess permittivity  $\epsilon_s^E$  as functions of  $x_{PC}$ . The dashed lines in (a) show the behaviors of ideal mixtures based on the Eyring formula, while the dashed lines in (b) mark the linear transition of from the cases of pure alcohol to pure PC.

## VI. Molecular Dynamic (MD) Results: RDF Analysis



**Fig. 6.** Radiation distribution functions (RDFs) of PC-MeOH mixtures with various PC concentrations. (a) O1(PC)-H(MeOH), (b) H(MeOH)-H(MeOH)



**Fig. 7.** Radiation distribution functions (RDFs) of PC-EtOH mixtures with various PC concentrations. (a) O1(PC)-H(EtOH), (b) H(EtOH)-H(EtOH)