Temperature Dependence of Physical Constants of Monofluorinated Propylene Carbonate as Highly Polar Liquid

Noritoshi Nanbu,*[1] Kazuki Takimoto,[1] Keita Suzuki,[1] Manabu Ohtake,[1] Kousuke Hagiyama,[1]
Masahiro Takehara,[2] Makoto Ue,[2] and Yukio Sasaki[1]
[1]*Department of Nanochemistry, Faculty of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi 243-0297*
[2]*Mitsubishi Chemical Group Science and Technology Research Center, Inc., 8-3-1 Chuo, Ami, Inashiki 300-0332*

(Received December 28, 2007; CL-071447; E-mail: nanbu@nano.t-kougei.ac.jp)

We describe the temperature dependence of relative permittivity (ε_r), mass density (ρ), refractive index (n_D), and dynamic viscosity (η) of monofluorinated propylene carbonate (FPC) as a highly polar liquid. The physical properties are compared with those of propylene carbonate (PC). The value of ε_r of FPC is as large as 196 even at 20 °C. The ρ and η of FPC are also much higher than those of PC.

Fluorine is the most electronegative of all the elements, and the size is small next to hydrogen. Fluorine atoms show very low polarizability and high enthalpy of ionization. Accordingly, partial fluorination of organic solvents exerts the strong polar effect on the physical properties such as permittivity, density, and viscosity.[1]

Cyclic carbonates are long-term commercially available solvents used in many industrial applications[2] such as cleaning/degreasing, paint stripping, gas treating, textile dyeing, electrochemical devices, etc. Propylene carbonate (PC) (4-methyl-1,3-dioxolan-2-one) is a typical cyclic carbonate. The dipole moments of cyclic carbonates are much higher than those of chain carbonates. The planarity of the 1,3-dioxolan-2-one moiety produces the vector addition of local dipoles which contribute to the overall dipole moment.

In this paper, we report the temperature dependence of relative permittivity, mass density, refractive index, and dynamic viscosity of monofluorinated propylene carbonate (FPC) (4-fluoromethyl-1,3-dioxolan-2-one). The relative permittivity is a very critical quantity in determining conductivity of a dilute electrolytic solution, because the degree of ionic dissociation of an electrolyte depends on permittivity of the medium. The electric dipole moment of the FPC molecule is estimated from the temperature dependence of the relative permittivity and the mass density.

We synthesized FPC from PC and molecular fluorine in the same manner as direct fluorination of γ-butylolactone[3] and dimethyl carbonate.[4] An aqueous solution of Na_2CO_3 was used to remove HF from the reaction mixture. FPC was purified under reduced pressure first by simple distillation and then by fractional distillation. FPC was identified by using gas chromatography coupled with mass spectrometry (GC-MS analysis) (Shimadzu Corp., GCMS-QP2010) and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy (JEOL Ltd., JNM-LA500).[5] The purity of FPC was determined to be more than 99.9% by means of gas chromatography equipped with a FID detector (Shimadzu Corp., GC-1700) and a TC-WAX (GL Sciences Inc., 0.25 mmϕ × 30 m, df = 0.25 µm). FPC was dehydrated with purified molecular sieves 4A before use. PC was used as received (Kishida Chemical Co., Ltd., LBG grade). The apparatus and techniques for measurements of the physical constants are essentially the same as those previously reported.[1]

Relative permittivity (ε_r) reflects the ease of dielectric polarization, and the strong attractive forces between solvent molecules lead to the increase in ε_r. ε_r has a very significant effect on the strength of the interactions between ions in an electrolytic solution. Figure 1a shows the θ dependence of ε_r. ε_r decreased gradually with an increase in θ. The great thermal motion of FPC and PC overcomes the mutual orientating effects of the dipoles at high θ. It should be noted that the value of ε_r of FPC is as large as 196 even at 20 °C. The ε_r of FPC is two to three times higher than that of common cyclic carbonates.[6] Monofluorination of the methyl group increases ε_r more markedly than that of the 1,3-dioxolan-2-one moiety. Dipole–dipole interactions involving the intermolecular hydrogen bonding (C–H···F–C or CF–H···O=C) are responsible for the cooperative orientation of the FPC molecules. Monofluorination of PC increases the amount of the dielectric polarization but may decrease the electron-pair donicity of oxygen atoms in the –OCOO– moiety. The low electron-pair donicity weakens solvation of cations such as alkaline metal ions.

The electric dipole moment of the molecule (μ) is calculated from the temperature dependence of ε_r and ρ by using the following Kirkwood's formula: $f(\varepsilon_r, \rho) \equiv (M/\rho)(\varepsilon_r - 1)(2\varepsilon_r + 1)/9\varepsilon_r = N_A(\alpha + g\mu^2/3kT)/3\varepsilon_0$, where ε_0, α, g, k, and T denote permittivity of vacuum, polarizability, Kirkwood's correlation factor, Boltzmann constant, and thermodynamic temperature, respectively. This Kirkwood's formula is expressed in International System of Units. The approximate expression for g can be derived only when nearest-neighbor interactions are considered; then $g = 1 + z\langle\cos\gamma_{ij}\rangle$, where γ_{ij} depends only on the coupled orientations of the i th and j th molecules, each with z nearest neighbors. If the value of g is taken as 3, then μ of FPC and PC is calculated to be 11.4 D (=3.79 × 10^{-29} C m) and 4.33 D (=1.45 × 10^{-29} C m), respectively, from the slopes of $f(\varepsilon_r, \rho)$ vs. T^{-1} plots (Figure 1b).

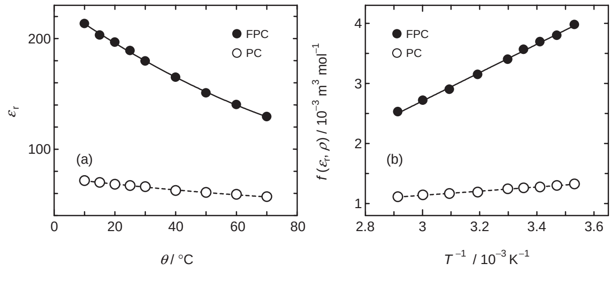

Figure 1. Plots (a) ε_r vs. θ and (b) $f(\varepsilon_r, \rho)$ vs. $1/T$ of FPC and PC from 10 °C (283.15 K) to 70 °C (343.15 K).

Copyright © 2008 The Chemical Society of Japan

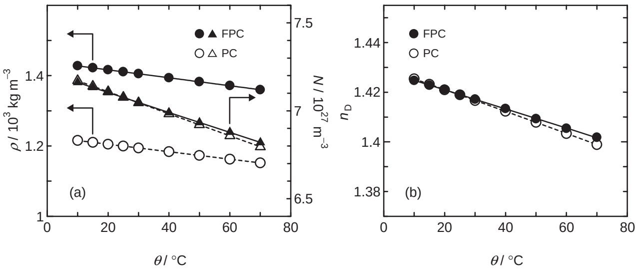

Figure 2. (a) ρ and N and (b) n_D of FPC and PC as a function of θ from 10 to 70 °C. N is calculated from ρ, M, and N_A according to $N = \rho N_A/M$.

The datum obtained for PC is close to the reported values (4.94^{7a} and 4.9^{7b} D). The g value of 3 indicates that two polar molecules are alined to form a head-to-tail dimer ($z = 2$ and $\gamma_{ij} = 0$).

Figure 2a shows the temperature (θ) dependence of mass densities (ρ) of FPC and PC. Figure 2a also depicts the θ dependence of the number densities of molecules (N). N refers to the number of molecules per unit volume and is calculated from ρ, molar mass (M), and Avogadro constant (N_A) according to the following equation: $N = \rho N_A/M$. Plots of ρ or N against θ are found to be linear. Both molecular mass ($=M/N_A$) and N are key factors determining ρ. Despite the larger molecular size, N of FPC was slightly higher than that of PC at high θ. The finding indicates that the strong attractive forces between FPC molecules cause a contraction in volume. N of common cyclic carbonates decreases in the reverse order of the molecular size.[6] ρ of FPC was considerably higher than that of PC. Molecular weights of FPC and PC are 120.08 and 102.09, respectively. Therefore, the difference in ρ between FPC and PC mainly reflects that in the molecular mass (m).

Refractive index (n_D) is related to the propagation speed of light in a medium and is a measure of the ability to bend (refract) light rays. Figure 2b shows the θ dependence of n_D. The data followed straight lines. In analogy with N, n_D of FPC was slightly higher than that of PC at high θ. Electronic polarizability (α_e) of the molecule as well as N are dominant factors governing n_D. α_e is obtained by the following Lorentz–Lorenz equation:[8] $(M/\rho)({n_D}^2 - 1)/({n_D}^2 + 2) = N_A\alpha_e/3\varepsilon_0$. The averages of α_e at 10–70 °C were nearly identical to each other: $9.48 \times 10^{-40}\,C^2\,m^2\,J^{-1}$ for FPC and $9.47 \times 10^{-40}\,C^2\,m^2\,J^{-1}$ for PC. The θ dependence of n_D of partially fluorinated chain carbonates is also the same as that of N.[1]

Dynamic viscosity (η) is regarded as an internal friction based on intermolecular forces. Figure 3 shows η as a function of (a) θ or (b) T. η decreases with an increase in temperature, and plots of $\log(\eta/\text{mPa s})$ vs. T^{-1} gave straight lines. The high translational kinetic energy allows intermolecular attractions to be overcome more easily, and the internal friction is reduced at high temperatures. The apparent activation energy for viscosity ($E_{a,\eta}$) is obtained from the relation proposed by Andrade:[9] $\eta = A_\eta \exp(E_{a,\eta}/RT)$. $E_{a,\eta}$ is determined to be 27.7 kJ mol^{-1} for FPC and 17.0 kJ mol^{-1} for PC. The η and $E_{a,\eta}$ of FPC are much higher than those of PC. The increase in both polarity and molecular mass exerts the synergistic effect on the η and $E_{a,\eta}$ of FPC.

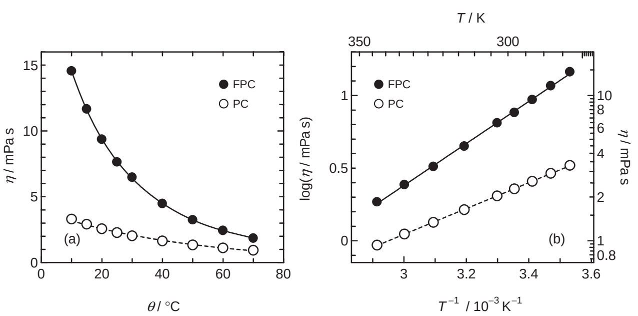

Figure 3. η of FPC and PC as a function of (a) θ or (b) T from 10 °C (283.15 K) to 70 °C (343.15 K).

In conclusion, monofluorination of PC greatly enhanced ε_r as well as ρ and η. The molecular properties (μ and m) rather than N have a strong influence on ε_r, ρ, and η of the highly polar liquid. Conductivity of a FPC solution is expected to be higher than that of the PC counterpart at least at low concentrations of electrolyte ions.

References and Notes

1 N. Nanbu, M. Takehara, S. Watanabe, M. Ue, Y. Sasaki, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1302.

2 J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663.

3 Y. Sasaki, R. Ebara, N. Nanbu, M. Takehara, M. Ue, *J. Fluorine Chem.* **2001**, *108*, 117.

4 M. Takehara, S. Watanabe, N. Nanbu, M. Ue, Y. Sasaki, *Synth. Commun.* **2004**, *34*, 1367.

5 GC-MS (EI) (m/z): 120 M^+ (4), 87 $C_3H_3O_3^+$ (100), 43 $C_2H_3O^+$ (62), 33 CH_2F^+ (14), 28 CO^+ (20), 27 $C_2H_3^+$ (14). ^{1}H NMR ($CDCl_3$, 500.00 MHz): δ 4.34 (m, 1H), 4.56–4.61 (m, 2H), 5.07 (d, 2H, $J = 3$ Hz). ^{13}C NMR ($CDCl_3$, 125.65 MHz): δ 65.01 (d, $J = 8$ Hz), 75.03 (d, $J = 18$ Hz), 82.33 (d, $J = 171$ Hz), 154.78 (s). ^{19}F NMR (C_6F_6, 470.40 MHz): δ −162.00 (1 F).

6 K. Hagiyama, K. Suzuki, M. Ohtake, M. Shimada, N. Nanbu, M. Takehara, M. Ue, Y. Sasaki, *Chem. Lett.* **2008**, *37*, 210.

7 a) *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed., ed. by J. A. Riddick, W. B. Bunger, T. K. Sakano, Wiley-Interscience, New York, **1986**, pp. 434–435. b) D. R. Lide, *Handbook of Organic Solvents*, CRC press, Boca Raton, **1995**, p. 412.

8 *Intermolecular & Surface Forces*, 2nd ed., ed. by J. N. Israelachvili, Academic Press, London, **1994**, Chap. 5, pp. 79–81; *Molecular Quantum Mechanics*, 3rd ed., ed. by P. W. Atkins, R. S. Friedman, Oxford, New York, **1997**, Chap. 12, pp. 397–401; *The Properties of Solvents*, ed. by Y. Marcus, John Wiley & Sons, Chichester, **1998**, Chap. 3, pp. 103–104.

9 E. N. Andrade, *Nature* **1930**, *125*, 309.

Published on the web (Advance View) April 5, 2008; doi:10.1246/cl.2008.476