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Polar Effect of Successive Fluorination of Dimethyl Carbonate on Physical Properties

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Successive fluorination of dimethyl carbonate (DMC) exerts a polar effect on various fundamental properties. We describe the temperature dependence of the mass density (ρ), refractive index (n_D), relative permittivity (ε_r), dynamic viscosity (η), and kinematic viscosity (ν) of trifluorinated, difluorinated, and monofluorinated DMCs (TFDMC, DFDMC, and MFDMC, respectively). η decreased in essentially the same order as ε_r: DFDMC > TFDMC > MFDMC > DMC. However, ν and the boiling point of the TFDMC were lower than those of the MFDMC.

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. Therefore, partially fluorinated solvents can exert a strong polar effect on various properties, unlike polyfluorinated and perfluorinated solvents. The polarity of the polyfluorinated and perfluorinated solvents is very low. They are the so-called fluorous media and are often immiscible with organic solvents as well as water.[1–3]

Dimethyl carbonate (DMC) is a chain carbonate and is commonly used as a low-viscosity solvent for electrochemical energy-storage devices, such as lithium-ion batteries.[4–7] Recently, Smart et al. have reported several trifluorinated chain carbonates, such as methyl 2,2,2-trifluoroethyl carbonate, and showed that the use of them as co-solvents improves the performance of lithium-ion cells.[8] However, there are scarcely any systematic and detailed studies reported on the fundamental properties of partially fluorinated chain carbonates, except for ours.[9–12]

In this paper, we report the polar effect of successive fluorination of DMC on the physical properties, such as mass density (ρ), refractive index (n_D), relative permittivity (relative dielectric constant, ε_r), dynamic viscosity (viscosity coefficient, η), kinematic viscosity (ν), and boiling point.

Experimental

Materials. Trifluorinated carbonate (TFDMC, difluoromethyl fluoromethyl carbonate), difluorinated carbonate (DFDMC, bis(fluoromethyl) carbonate), and monofluorinated carbonate (MFDMC, fluoromethyl methyl carbonate) were synthesized by direct fluorination of DMC[13] (Chart 1) and were purified by simple distillation followed by fractional distillation at atmospheric pressure. TFDMC was isolated from the reaction mixture in this work. However, the fraction of the TFDMC estimated from the gas chromatogram was less than 10%. The boiling point of the TFDMC (100 °C) was close to that of the MFDMC (108 °C). Therefore, separation by two types of distillation greatly decreased the total yield of the TFDMC. The purity of TFDMC, DFDMC, and MFDMC was determined to be 99.0, 99.5, and 99.7%, respectively, by means of gas chromatography (Shimadzu, GC-1700). DMC (Kishida, battery grade) was used as received. TFDMC, DFDMC, and MFDMC were dehydrated with purified molecular sieves 4A before use.

The TFDMC, the DFDMC, and the MFDMC were identified by using gas chromatography coupled with mass spectrometry (GC-MS analysis) (JEOL, JMS-SX102A) and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy (JEOL, JNM-LA500). The results are as follows: GC-MS (CI) (m/z): MFDMC, 109 $[M+H]^+$; DFDMC, 127 $[M+H]^+$; TFDMC, 145 $[M+H]^+$. GC-MS (EI) (m/z): MFDMC, 77

Dimethyl carbonate (DMC)

Monofluorinated dimethyl carbonate
(MFDMC, Fluoromethyl methyl carbonate)

Difluorinated dimethyl carbonate
(DFDMC, Bis(fluoromethyl) carbonate)

Trifluorinated dimethyl carbonate
(TFDMC, Difluoromethyl fluoromethyl carbonate)

Chart 1.

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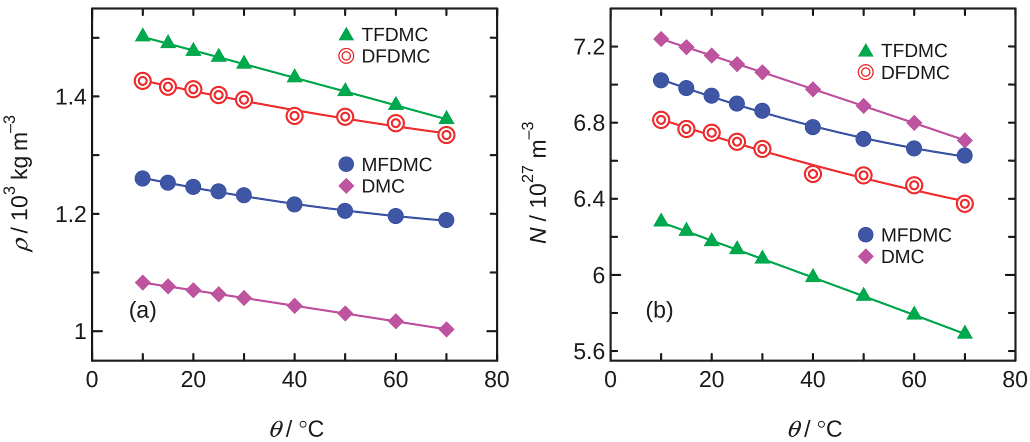

Fig. 1. (a) ρ and (b) N of TFDMC, DFDMC, MFDMC, and DMC as a function of θ from 10 to 70 °C. N was calculated from ρ, molar mass, and N_A according to Eq. 1.

$COOCH_2F^+$ (4.33), 59 $COOCH_3^+$ (84.25), 33 CH_2F^+ (100); DFDMC, 77 $COOCH_2F^+$ (15.74), 33 CH_2F^+ (100); TFDMC, 33 CH_2F^+ (46.27), 51 CHF_2^+ (100), 77 $COOCH_2F^+$ (7.05), 95 $COOCHF_2^+$ (3.52). ^{1}H NMR (TMS/$CDCl_3$, 500.00 MHz): MFDMC, δ 4.23 (s, 3H), 6.08 (d, $^2J_{HF} = 51.5$ Hz, 2H); DFDMC, δ 6.04 (d, $^2J_{HF} = 50$ Hz, 2H); TFDMC, δ 6.05 (d, $^2J_{HF} = 49$ Hz, 2H), 7.34 (t, $^2J_{HF} = 71$ Hz, 1H). ^{13}C NMR (TMS/$CDCl_3$, 125.65 MHz): MFDMC, δ 55.10, 96.97 (d, $^1J_{CF} = 219$ Hz), 154.68; DFDMC, δ 97.28 (d, $^1J_{CF} = 223$ Hz), 152.97; TFDMC, δ 97.17 (d, $^1J_{CF} = 225$ Hz), 114.13 (t, $^1J_{CF} = 260$ Hz), 149.90 (t, $^3J_{CF} = 5$ Hz). ^{19}F NMR (CF_3COOD/D_2O, 470.40 MHz): MFDMC, δ -158.05 (t, $^2J_{FH} = 51.5$ Hz, 1F); DFDMC, δ -159.70 (t, $^2J_{FH} = 50$ Hz, 1F); TFDMC, δ -92.75 (d, $^2J_{FH} = 71$ Hz, 2F), -160.44 (t, $^2J_{FH} = 49$ Hz, 1F).

Apparatus and Measurements. The temperature in a TC-WAX capillary column for gas chromatography was increased at a rate of 10 °C min^{-1} from 50 to 100 °C.[13] ρ was measured by use of density/gravity meters (Kyoto Electronics, DA300 and DA-310). n_D was determined on an Abbe refractometer (model 2_T) equipped with a jacket. Water supplied from a constant-temperature bath was circulated through the jacket. ε_r was measured by using a LF impedance analyzer (Hewlett Packard, 4192A) connected to a thermostat (Ando Denki, TO-9). The electrostatic capacitance of air (C_0) and sample (C_{sample}) was measured at a frequency of 1 MHz, and ε_r was approximated by the ratio C_{sample}/C_0. The samples were deaerated by bubbling Ar gas (99.9%) before the measurements. ν was measured by using a capillary-tube viscometer, Ostwald viscometer (Shibayama), immersed in a thermostat. η was determined as $\nu \cdot \rho$; ν is defined as η/ρ and is directly proportional to the time required for the liquid to flow through a capillary-tube viscometer under its own hydrostatic head. The physical properties of TFDMC, DFDMC, MFDMC, and DMC were investigated over the temperature range of 10 to 70 °C.

Results and Discussion

Mechanical Properties. Figure 1 shows the Celsius-temperature (θ) dependence of (a) ρ and (b) number density of molecules (N) of TFDMC, DFDMC, MFDMC, and DMC. 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:

$$N = \frac{\rho N_A}{M}. \tag{1}$$

The θ dependence of N has a pronounced contribution to the change in physical constants, as described later. ρ decreased in the same order as the molecular weight: TFDMC (144.05) > DFDMC (126.06) > MFDMC (108.07) > DMC (90.08). However, N decreased in the inverse order. In general, as the molecular weight increases, so too does the molecular size. The increase in the molecular size results in the decrease in N.

Optical and Electric Properties. The θ dependence of n_D of the four chain carbonates is depicted in Fig. 2a. 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. The feature of n_D was similar to that of N. Successive fluorination of DMC resulted in a lower N and, consequently, in lower n_D. n_D depends on both electronic polarizability or dynamic polarizability (α_e) of the molecules and N. This is because the propagation of light through a medium can be imagined to occur by the incident light inducing an oscillating dipole moment, which then radiates light of the same frequency.

α_e is obtained by the following Lorentz–Lorenz equation:[14–16]

$$\frac{{n_D}^2 - 1}{{n_D}^2 + 2} \cdot \frac{M}{\rho} = \frac{N_A \alpha_e}{3\varepsilon_0}, \tag{2}$$

where ε_0 is permittivity of vacuum. The average of α_e at 10–70 °C decreased in the following order: TFDMC (8.593×10^{-40} C^2 m^2 J^{-1}) > DFDMC (8.426×10^{-40} C^2 m^2 J^{-1}) > DMC (8.346×10^{-40} C^2 m^2 J^{-1}) > MFDMC (8.309×10^{-40} C^2 m^2 J^{-1}). α_e can depend on the molecular mass and the frequency of an applied electric field unlike the static polarizability.[15] Difluorination and trifluorination of DMC increased α_e as compared to the DMC. Interestingly, despite the increase of the molecular mass, monofluorination of the DMC caused a slight decrease in α_e. It is well-known that n_D of polyfluorinated and perfluorinated compounds, which may have a considerably lower N, is lower than those of the corresponding fluorine-free compounds.

Figure 2b shows the θ dependence of ε_r of the four chain

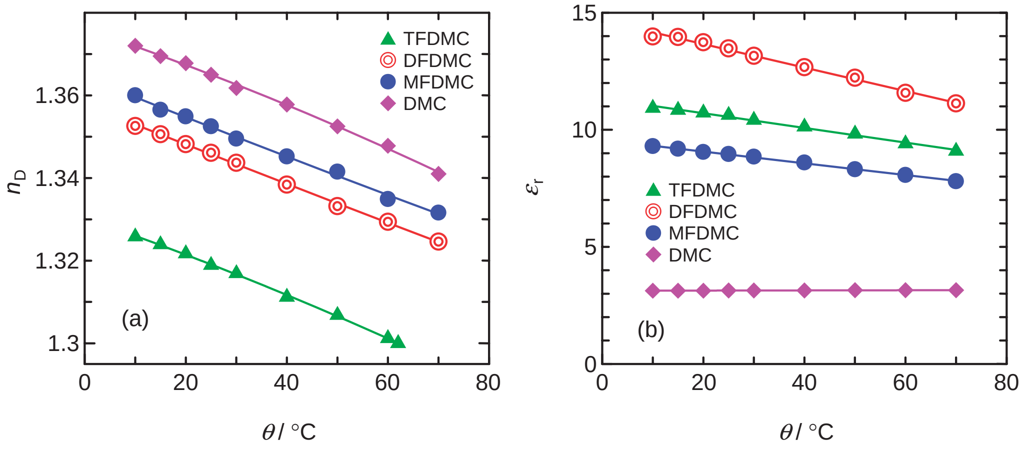

Fig. 2. (a) n_D and (b) ε_r of TFDMC, DFDMC, MFDMC, and DMC as a function of θ from 10 to 70 °C.

carbonates. ε_r is characterized by the ease of dielectric polarization and has a very significant effect on the strength of the interactions between ions in an electrolytic solution. ε_r decreased in the following order: DFDMC > TFDMC > MFDMC > DMC. ε_r of the DFDMC, the TFDMC, and the MFDMC decreased linearly with an increase in θ. In contrast, ε_r of the DMC increased only slightly with θ, suggesting that molecular association, which cancels out dipole moments, takes place at low θ like acetic acid. Vectorial addition of the dipole moments associated with the presence of electronegative fluorine and oxygen atoms indicates that the resultant electric dipole moments of the DFDMC and the TFDMC molecule are higher than that of the MFDMC molecule. ε_r of the DFDMC was higher than that of the TFDMC. Peaks appearing on ^{1}H and ^{19}F NMR spectra were shifted to higher and lower frequencies, respectively, when fluorine atoms were introduced into DMC. The ^{1}H and ^{19}F NMR data indicate that successive fluorination of the DMC decreases the electron density of the hydrogen atom and increases that of the fluorine atom. These findings suggest that the participation of the intermolecular hydrogen bonding (C–H···F–C) is a key factor determining the order of ε_r. The number of hydrogen atoms that are attached to the same carbon atom as fluorine atoms decreases in the following order: DFDMC (4) > TFDMC (3) > MFDMC (2) > DMC (0). Partial fluorination of the DMC can increase the polarity, though the extent depends on both the number of fluorine atoms and the position where the substitution takes place (symmetry). Dipole–dipole interactions involving the intermolecular hydrogen bonding are responsible for the cooperative orientation of the partially fluorinated DMC molecules, which results in the increase in ε_r at lower θ. Successive fluorination of the DMC can decrease the electron-pair donicity of oxygen atoms in the OCOO moiety, and the low electron-pair donicity can weaken solvation of cations such as lithium ion.

Figure 3 compares ε_r with the square of n_D. The values of ε_r of the four chain carbonates were higher than predicted by the Maxwell-derived equation $\varepsilon_r = n_D{}^2$. Orientation, atomic, and electronic polarization can contribute to ε_r at a frequency of 1×10^6 Hz, while n_D measured at a frequency of 5.0876×10^{14} Hz (light of the D-line of the sodium spectrum, wavelength (λ) = 589.26 nm) may involve only electronic polarization.[16,17] The amount of the orientation polarization decreases with an increase in θ. Even ε_r of a nonpolar liquid is higher than the square of n_D, because ε_r can result from atomic polarization as well as electronic polarization.

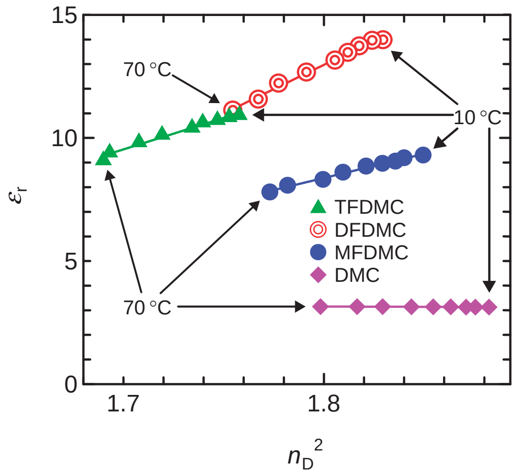

Fig. 3. Comparison between ε_r and $n_D{}^2$ of TFDMC, DFDMC, MFDMC, and DMC.

Transport Properties. Figure 4 shows (a), (c) η and (b), (d) ν of the four chain carbonates as a function of θ or thermodynamic temperature (T). η and ν decreased with an increase in the temperature, and plots of $\log(\eta/\text{mPa s})$ or $\log(\nu/10^{-6}\,\text{m}^2\,\text{s}^{-1})$ vs. T^{-1} gave straight lines. η decreased in essentially the same order as ε_r: DFDMC > TFDMC > MFDMC > DMC. η can be regarded as an internal friction based on intermolecular forces and can be governed by the mass, rigidity, size, and shape of the molecule as well as the dipole moment and the static polarizability.

ν is defined as the ratio of η to ρ of a fluid. Liquids of high viscosity have high boiling points. The order of ν near room temperature agreed with that of the boiling points: DFDMC (120 °C) > MFDMC (108 °C) > TFDMC (100 °C) > DMC (90 °C). The order observed for MFDMC and TFDMC was the reverse of that of η. The value of ν of TFDMC was lowest at high θ. Since both η and ρ are correlated with the molecular mass, the resulting ν may not be appreciably affected by it. Therefore, the difference in ν becomes smaller than that in η, and the order of ν can change. ν can more explicitly reflect

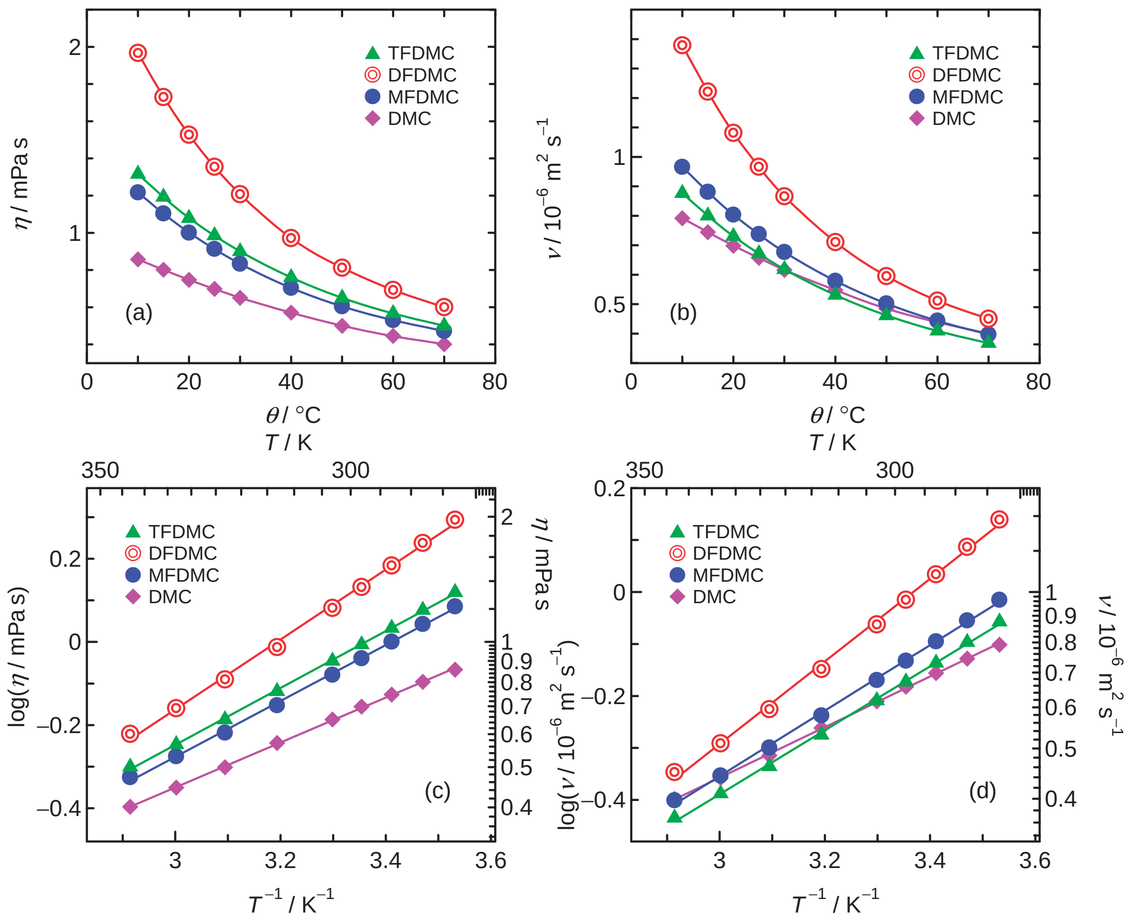

Fig. 4. (a), (c) η and (b), (d) ν of TFDMC, DFDMC, MFDMC, and DMC as a function of θ or T from 10 °C (283.15 K) to 70 °C (343.15 K).

the intermolecular forces. Partial fluorination of the DMC increases the dipole–dipole interactions, because the net dipole moment of the molecule increases. On the other hand, polyfluorination or perfluorination may decrease the dispersion or London interactions because of low polarizability of the fluorine atoms. A suitable balance of the intermolecular forces, including the dipole–dipole, the dipole–induced-dipole, and the induced-dipole–induced-dipole interactions (so-called van der Waals forces), can determine the order of ν.

A higher translational kinetic energy can allow intermolecular attractions to be overcome more easily, and the internal friction is reduced at high temperatures. The apparent activation energy for viscosity ($E_{a,\eta}$), which was obtained from the relation proposed by Andrade,[18] was 16.10, 13.10, 12.87, and 10.35 kJ mol^{-1} for DFDMC, TFDMC, MFDMC, and DMC, respectively.

$$\eta = A_\eta \exp\left(\frac{E_{a,\eta}}{RT}\right). \tag{3}$$

The order of the $E_{a,\eta}$ was also in accord with that of η. The higher $E_{a,\eta}$ of the partially fluorinated DMCs indicates that η and ν decrease rapidly at high temperatures.

A *gem*-difluoride of DMC, difluoromethyl methyl carbonate (*gem*-DFDMC), in which two fluorine atoms and an oxygen atom are attached to the same carbon atom, is isomeric with the DFDMC. Although *gem*-DFDMC is also generated by direct fluorination of DMC,[13] we could not isolate it from the reaction mixture. We found that the boiling point of the *gem*-DFDMC was as low as 85 °C.[13] ν of the TFDMC was lower than that of the MFDMC over the θ range investigated, as described above. These findings support the idea that the bonding of two fluorine atoms and an oxygen atom to the same carbon atom can weaken the intermolecular forces and that ν of the *gem*-DFDMC may be very low.

Influence of Number Density of Molecules on Physical Constants. The values of ρ, n_D, ε_r, η, and ν of the four chain carbonates gradually decreased with increasing θ except for ε_r of DMC, which had the lowest polarity. As θ increases, the thermal motion of the molecules becomes vigorous. The greater thermal motion results in a lower N. ρ is correlated with both the molecular mass and N. The value of n_D depends on both α_e of the molecules and N. The molecular mass and α_e are independent of θ. Therefore, the θ dependence of ρ and n_D is simply determined by that of N.

Dipole moments and static polarizability are essential for the interpretation of the intermolecular forces. These molecular properties rather than N may have a strong influence on ε_r, η, and ν of polar liquids. The greater thermal motion overcomes the mutual orientating effects of the dipoles at high θ.

Conclusion

The use of the simple chain carbonates allows us to investigate the polar effect of successive fluorination on various properties in detail. The trade-off between high electronegativity (excellent electron withdrawal) and low polarizability of fluorine atoms plays a significant role in determination of the magnitude of the polar effect.

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