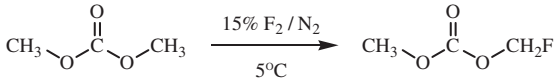
Physical Properties of Monofluorodimethyl Carbonate

Masahiro Takehara, Susumu Watanabe, Noritoshi Nanbu*, Makoto Ue,† and Yukio Sasaki*
Department of Applied Chemistry, Faculty of Engineering, Tokyo Polytechnic University
(Former name: Tokyo Institute of Polytechnics), 1583 Iiyama, Atsugi 243-0297
†*Mitsubishi Chemical Group Science and Technology Research Center, Inc., 8-3-1 Chuo, Ami, Inashiki 300-0332*

(Received November 4, 2003; CL-031045)

Partial fluorination of solvents can improve various physical properties because of the polar effect. We have investigated the temperature dependence of relative permittivity (ε_r), viscosity (η), refractive index (n_D), and density (ρ) of monofluorodimethyl carbonate (MFDMC) over a range of 10 to 70 °C and compared the physical properties with those of dimethyl carbonate (DMC). The ε_r, η, and ρ of the MFDMC are higher than those of the DMC, whereas the n_D becomes lower.

A fluorine atom is highly electronegative and shows a very low electronic polarizability and high enthalpy of ionization. Therefore, partially fluorinated solvents can exert the strong polar effect on physical properties such as relative permittivity and viscosity, as distinct from those of polyfluorinated or perfluorinated solvents. However, to our knowledge, there is no report of the physical properties of partially fluorinated chain esters. Dimethyl carbonate (DMC) is one of the low-viscosity chain esters commonly used in such electrochemical energy storage devices as lithium batteries.[1–3] In the present paper, we report the temperature dependence of relative permittivity (ε_r), viscosity (η), refractive index (n_D), and density (ρ) of monofluorodimethyl carbonate (MFDMC), which we have newly developed, from 10 to 70 °C. These physical properties are compared with those of the DMC.



DMC MFDMC

MFDMC was synthesized similarly to fluorinated γ-butyrolactones[4] by direct fluorination and purified by fractional distillation at atmospheric pressure. We have isolated the MFDMC from the fluorinated DMC sample in a 45% yield. Since this yield was essentially the same as that of the MFDMC formed by the direct fluorination of the DMC, almost all of the MFDMC formed was successfully separated. The MFDMC was identified by techniques of gas chromatography coupled with mass spectrometry (GC–MS analysis),[5] elemental analysis,[6] and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[7] The purity of the MFDMC was determined to be 99.7% by means of gas chromatography (GC-1700, SHIMADZU). The apparatus and techniques for measurements of relative permittivity, viscosity, density, and refractive index are described elsewhere.[8,9] The physical properties of MFDMC and DMC were measured from 10 to 70 °C.

Figure 1 shows the temperature dependence of (a) relative permittivity, ε_r, (b) viscosity, η, and (b) kinematic viscosity, ν, of MFDMC and DMC. The ε_r of the MFDMC was higher than that of the DMC and decreased linearly with temperature, θ. On the other hand, the ε_r of the DMC was almost independent of the θ over a range of 10 to 70 °C. These findings indicate that

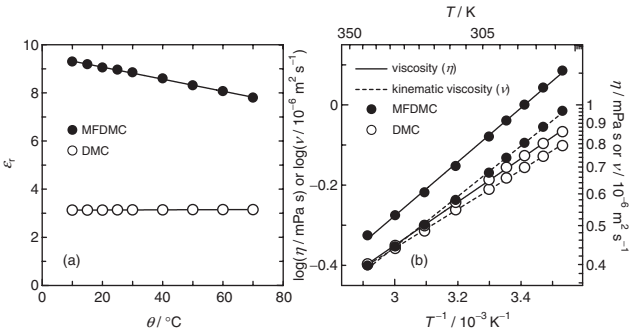


Figure 1. (a) Relative permittivity, ε_r, (b) viscosity, η, and (b) kinematic viscosity, ν, of MFDMC and DMC as a function of temperature, θ, from 10 to 70 °C.

the dipole–dipole interactions including the intermolecular hydrogen bonding in the MFDMC system is stronger than that in the DMC system.

The electric dipole moment of the DMC is considerably lower than those of cyclic esters such as ethylene carbonate (EC) and propylene carbonate (PC). The cyclic nature of the EC and the PC constrains –OCH_2– moieties to align in a planar geometry (*cis* orientation). Since the methoxy groups of the DMC can readily rotate about the CO bond and avoid the sterically hindered planar configuration, the two identical groups in the molecule orient in the energetically more stable *trans* configuration.[1,3] The lack of the planarity for the DMC molecule produces a partial cancellation of local electric dipole moments. The partial cancellation results in very low polarity, namely the small overall electric dipole moment and low ε_r, of the DMC. Since a fluorine atom is highly electronegative, a local dipole moment ascribable to a fluoromethoxy group, CH_2FO–, in the MFDMC molecule, would more than compensate for the partial cancellation. Accordingly, the polarity of the MFDMC molecule becomes higher than that of the DMC molecule, and the dipole–dipole interactions including the intermolecular hydrogen bonding can be stronger.

The η of both chain esters decreased with an increase of absolute temperature, T, and plots of $\ln(\eta/\text{mPa s})$ vs $1/T$ gave straight lines. The η of MFDMC was higher than that of DMC. The finding is in accord with a simple expectation based on the increase of the ε_r, as distinct from fluorination of EC.[10] The η of monofluoriated and difluorinated ECs is higher than that of EC, but the ε_r becomes lower.

The η can be regarded as an internal friction and be governed by the size, surface area, and shape of the molecule as well as its polarity. In general, as the size and surface area of a molecule increase, so too does the dispersion or London interaction between the molecules. Thus, the larger size and surface area of the MFDMC molecule can lead to the increase of the η in co-

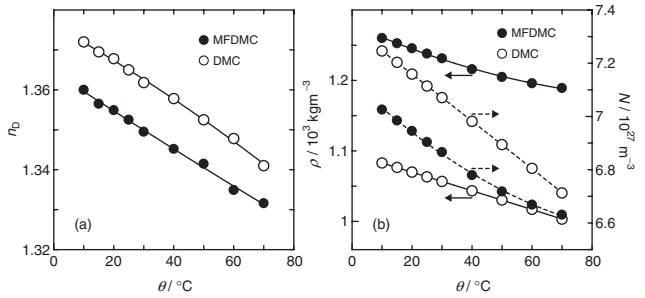


Figure 2. (a) Refractive index, n_D, (b) density, ρ, and (b) the number density of molecules, N, of MFDMC and DMC as a function of temperature, θ, from 10 to 70 °C. The N was calculated from the ρ, molar mass, and Avogadro's constant.

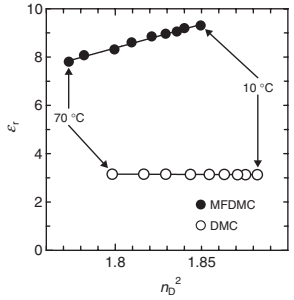


Figure 3. Comparison of ε_r and n_D^2 of MFDMC and DMC over a temperature range of 10 to 70 °C.

operation with the higher polarity. The apparent activation energies for viscosity, $E_{a,\eta}$, obtained from the relation proposed by Andrade[11] were 12.87 and 10.35 kJ mol^{-1} with regard to the MFDMC and the DMC, respectively. The higher η of the MFDMC can account for the increase of the $E_{a,\eta}$. Liquids of high viscosity have high boiling points. The boiling points of the MFDMC and the DMC are 108 and 90 °C, respectively.

The density of MFDMC was higher than that of DMC, as can be seen from Figure 2(b). The v of MFDMC was essentially the same as that of DMC at high temperatures, whereas the v of the MFDMC was higher at low temperatures. This finding indicates that the larger size of the MFOMC molecule makes them difficult to move at low temperatures.

Figure 2 shows the temperature dependence of (a) refractive index, n_D, and (b) density, ρ, of MFDMC and DMC. Moreover, the number density of molecules, N, i.e., the number of molecules per unit volume, which was calculated from the ρ, molar mass, and Avogadro's constant, is depicted in the figure (b). The ρ of the MFDMC was higher than that of the DMC. A fluorine atom makes the larger contribution to the mass of the MFDMC molecule than to the volume. The molecular weights of the MFDMC and the DMC are 108.07 and 90.08, respectively. The synergism of the higher molecular weight and higher polarity of the MFDMC can result in the increase of the ρ.

Interestingly, the n_D of the MFDMC was lower than that of the DMC, even though the MFDMC showed the higher ρ. The n_D is a measure of the ability to bend (refract) light rays and is related to both electronic polarizability, α_e, of the molecule and the 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. In spite of the larger molecular size, the average α_e of the MFDMC molecule, 8.309×10^{-40} C^{2}m^{2}J^{-1} (average polarizability $\alpha_e' = \alpha_e/4\pi\varepsilon_0 = 7.468 \times 10^{-30}$ m^3), obtained by Lorentz-Lorenz equation[12] was slightly lower than that of the DMC molecule, 8.346×10^{-40} C^{2}m^{2}J^{-1} ($\alpha_e' = 7.501 \times 10^{-30}$ m^3). The lower α_e of the MFDMC molecule can be ascribed to the low electronic polarizability of the fluorine atom. In addition, the N of the MFDMC was smaller than that of the DMC because of the larger size of the MFDMC molecule. The small number of the MFDMC molecules with the lower α_e is responsible for the decrease of the n_D. We would expect a similar argument to apply to n_D of polyfluorinated or perfluorinated solvents.

The ε_r, η, ρ, and n_D of the MFDMC and the DMC gradually decreased with increasing temperature except the ε_r of the DMC. As the temperature rises, the thermal motion of the molecules becomes vigorous. The greater thermal motion overcomes the mutual orientating effects of the dipoles at higher temperatures, and the internal friction is reduced. Therefore, the ε_r, η, and ρ can decrease. Since the N also decreases, the n_D can become lower.

Figure 3 shows a comparison of ε_r and the square of n_D. The values of the ε_r of both chain esters were higher than those of the n_D^2. The deviation of the ε_r from the relation expressed by $\varepsilon_r = n_D^2$ can result from atomic and orientation polarization,[13] because the ε_r and the n_D are measured at different frequencies of 1×10^6 Hz and 5.087×10^{14} Hz (for light of the D-line of the sodium spectrum, wavelength $\lambda = 589.3$ nm), respectively.

In conclusion, we have investigated the temperature dependence of ε_r, η, n_D, and ρ of MFDMC from 10 to 70 °C and have compared the physical properties with those of DMC. The MFDMC exerted the polar effect on the physical properties. The ε_r, η, and ρ of the MFDMC were higher than those of the DMC, whereas the n_D became lower. It is also very intriguing to investigate the physical properties of other fluorinated chain esters systematically.

References and Notes

1 L. A. Dominey, in "Lithium Batteries," ed. by G. Pistoia, Elsevier, Amsterdam (1994), Chap. 4.
2 M. Morita, M. Ishikawa, and Y. Matsuda, in "Lithium Ion Batteries," ed. by M. Wakihara and O. Yamamoto, KODANSYA and WILEY-VCH, Tokyo (1998), Chap. 7.
3 M. Salomon, H.-P. Lin, E. J. Plichta, and M. Hendrickson, in "Advances in Lithium-Ion Batteries," ed. by W. A. van Schalkwijk and B. Scrosati, Kluwer Academic/Plenum Publishers, New York (2002), Chap. 11.
4 Y. Sasaki, R. Ebara, N. Nanbu, M. Takehara, and M. Ue, *J. Fluorine Chem.*, **108**, 117 (2001).
5 GC–MS (CI) (m/z): 109 $[M+H]^+$. GC–MS (EI) (m/z): 77 $COOCH_2F^+$ (4.33), 59 $COOCH_3^+$ (84.25), 33 CH_2F^+ (100).
6 Anal. Calcd. for $C_3H_5FO_3$: C, 33.3; H, 4.7; F, 17.6%. Found: C, 33.4; H, 3.9; F, 17.5%.
7 ^{1}H NMR (1% TMS/$CDCl_3$, 500.00 MHz): δ 4.23 (s, 3H), 6.08 (d, $^2J_{HF} = 51.5$ Hz, 2H). ^{13}C NMR (1% TMS/$CDCl_3$, 125.65 MHz): δ 55.10, 96.97 (d, $^1J_{CF} = 219.0$ Hz), 154.68. ^{9}F NMR (2% CF_3COOD/D_2O, 470.40 MHz): δ −158.05 (t, $^2J_{FH} = 51.5$ Hz).
8 Y. Sasaki, T. Koshiba, H. Taniguchi, and Y. Takeya, *Nippon Kagaku Kaishi*, **1992**, 140.
9 M. Handa, M. Kataoka, M. Wakaumi, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **70**, 315 (1997).
10 M. Kobayashi, T. Inoguchi, T. Iida, T. Tanioka, H. Kumase, and Y. Fukai, *J. Fluorine Chem.*, **120**, 105 (2003).
11 E. N. Andrade, *Nature*, **125**, 309 (1930).
12 P. W. Atkins and R. S. Friedman, in "Molecular Quantum Mechanics," 3rd ed., Oxford, New York (1997), Chap. 12.
13 K. Izutsu, in "Electrochemistry in Nonaqueous Solutioins," WILEY-VCH, Weinheim (2002), Chap. 1.

Published on the web (Advance View) March 5, 2004; DOI 10.1246/cl.2004.338