

Physical and Electrochemical Properties of Partially Fluorinated Chain Carbonates

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Fluorine is the most electronegative of all the elements, and the size is small next to hydrogen. The fluorine atom shows a very low electronic polarizability and high enthalpy of ionization. Therefore, unlike polyfluorinated and perfluorinated solvents, partially fluorinated solvents can exert the strong polar effect on physical and electrochemical properties.

We report here the mass densities (ρ), refractive indexes (n_D), relative permittivities (ϵ_r), viscosity coefficients (η), and kinematic viscosities (ν) of monofluorodimethyl carbonate (MFDMC) and 2-fluoroethyl methyl carbonate (FEMC), which we have newly developed. Moreover, the specific conductivities (κ) and electrochemical stability of MFDMC and FEMC solutions containing LiPF_6 are investigated. The synthesis of the MFDMC¹⁾ and the FEMC²⁾ is described elsewhere.

Figure 1(a) shows the temperature (θ) dependence of the ρ and number density of molecules (N) of four chain carbonates. The ρ of the partially fluorinated chain carbonates was higher than that of the unsubstituted chain carbonates, as can be expected from the increase of molecular weights. Although the N of the MFDMC became lower than that of the DMC, that of the FEMC was higher than that of the EMC. A similar feature was observed for n_D (Figure 1(b)). The n_D depends on both electronic polarizability (α_e) of the molecule and the N . The larger number of the FEMC molecules is responsible for the increase of the n_D despite of its lower α_e .

The ϵ_r of the partially fluorinated carbonates was higher than that of the unsubstituted carbonates and decreased linearly with θ (Figure 1(c)). The ϵ_r of the unsubstituted carbonates was almost independent of the θ over a wide range of 10 to 60 °C. These findings indicate that permanent electric dipole moments of the partially fluorinated carbonates are higher than those of the unsubstituted carbonates and that the dipole-dipole interactions accompanying the intermolecular hydrogen bond in the former system are stronger. The ϵ_r of the four chain carbonates was higher than predicted by the expression $\epsilon_r = n_D^2$.

Figure 1(d) indicates that η of the four chain carbonates decreased with an increase of temperature (T) and that plots of $\log(\eta/\text{mPa s})$ vs. $1/T$ gave straight lines. The η of the partially fluorinated carbonates was higher than that of the unsubstituted carbonates. The finding is in accord with a simple expectation based on the increase of the ϵ_r . A similar feature was observed for ν , though the difference became smaller than that in the η .

Figure 2 shows the variations of κ of four chain carbonate solutions containing $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ with respect to θ . The κ of the MFDMC solution was lower than that for the DMC solutions over a temperature range of 10 to 60 °C, whereas that for the FEMC solution became higher than that for the EMC solution at 50 °C or more. This is because the η of the FEMC was greatly

diminished at high temperatures.

Linear potential sweep voltammograms (Figure 3) indicate that the stability to oxidative decomposition of partially fluorinated carbonates was slightly higher than that for the unsubstituted carbonates because of the introduction of a fluorine atom.

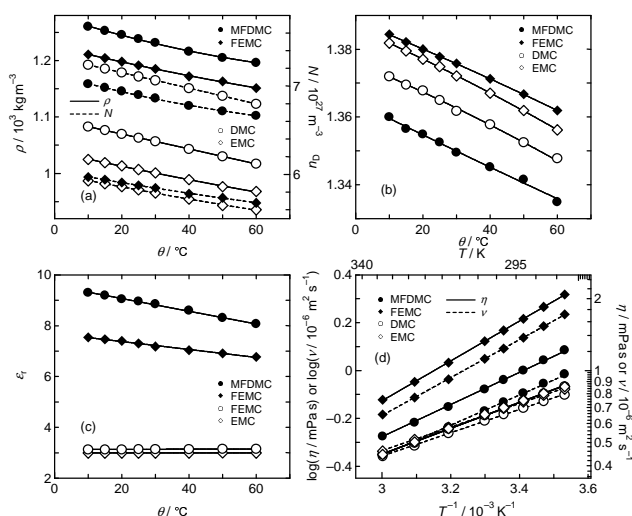


Fig. 1 (a) Mass densities (ρ) and the number densities of molecules (N); (b) refractive indexes (n_D); (c) relative permittivities (ϵ_r); and (d) viscosity coefficients (η) and kinematic viscosities (ν) of MFDMC, FEMC, DMC, and EMC as a function of temperature from 10 to 60 °C. The N was calculated from the ρ , molar mass, and Avogadro's constant.

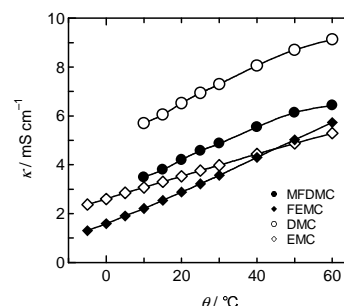


Fig. 2 Specific conductivities (κ) of MFDMC, FEMC, DMC, and EMC solutions containing $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ as a function of temperature (θ).

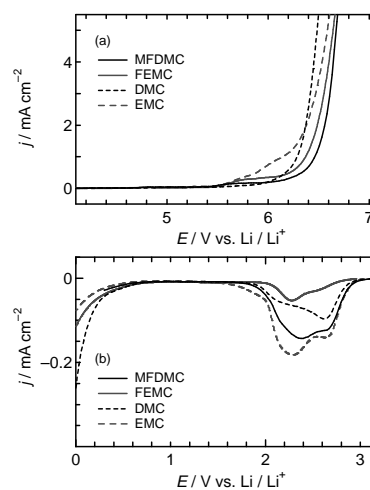


Fig. 3 Linear potential sweep voltammograms obtained for MFDMC, FEMC, DMC, and EMC solutions containing $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ with a Pt electrode at a scan rate of 5 mV s^{-1} at 25 °C.

References

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