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Notes

A pfg-NMR Investigation of the Diffusion Coefficients of Anionic Species in the System PPG4000−$LiCF_3SO_3$

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Following early work by Armand[1] on ionically conducting polyether−alkali metal salt complexes, *i.e.*, polymer electrolytes, research in this field is now motivated not only by the great potential of these materials in various electrochemical applications but also because of their intriguing transport properties.[2] Ionic transport occurs mainly in amorphous liquid-like regions of polymer−salt complexes based on high-molecular weight host polymers.[3] Low-molecular weight liquid polymers are therefore commonly used as model systems in fundamental studies of microscopic properties and transport processes.

In particular, poly(propylene glycol) of molecular weight 4000, PPG4000, has frequently been used in studies on the temperature and concentration dependence of the ionic conductivity[4] and also in vibrational spectroscopic studies of the cation−anion interactions.[5,6] Generally speaking, electrolytes based on PPG4000 exhibit a strong characteristic concentration dependence of the equivalent ionic conductivity Λ (ionic conductivity, σ, normalized to salt concentration), which increases from a minimum in dilute solutions passing through a maximum at high concentrations.[4]

We have previously reported Raman spectroscopic data on the concentration dependence of the distribution of ionic species in the PPG4000−$LiCF_3SO_3$ system, in an attempt to explain the conductivity behavior in terms of changes in the ionic speciation, *i.e.*, in terms of an increase in the relative abundance of available charge carriers with increasing concentration.[6] No significant changes could, however, be resolved over the concentration range corresponding to the observed increase in Λ, and the effect was attributed to an enhancement of the ionic mobility with increasing salt concentration.[6]

Recently, one of us has investigated the influence of relatively large densities of polar hydroxyl terminal groups in PPG4000 on the ionic speciation and conductivity in complexes of PPG4000 and $LiCF_3SO_3$ salt by using an endo-methylated PPG4000 host.[7,8] As a result it was concluded that the presence of hydroxyl groups does indeed influence the ionic speciation, and a specific interaction between $CF_3SO_3^-$ anions and hydroxyl end-groups was inferred from Raman spectroscopic data.[7] It was also found that the relative increase in Λ with increasing salt concentration was even more pronounced in the endo-methylated electrolyte.[8] Thus, it was concluded that the characteristic concentration behavior of Λ in the PPG4000-based electrolytes is not dominated by any saturation of preferred coordination sites associated with hydroxyl terminal groups.[7,8]

In this context we note that Prud'homme and co-workers[9,10] have suggested, on the basis of DSC data, that electrolytes based on PPG4000 are characterized by a microscopic phase separation and that the strong concentration dependence of the ionic conductivity may be attributed to this phase-segregated morphology.

In view of the proposed enhancement of the ionic mobility with increasing salt concentration in the PPG4000−$LiCF_3SO_3$ system,[6] we here report pfg-NMR data on the concentration dependence of the self-diffusion coefficients of anionic species and compare the results with viscosity data previously published for the same electrolytic solution.[4]

Experimental Section

Polymer electrolytes were prepared by complexing PPG4000 (Polysciences) with $LiCF_3SO_3$ (Aldrich Chemical Co. Inc.) for concentrations in the ether oxygen to lithium cation ratio (O:Li) range 495:1 to 23:1 (corresponding to the concentration range 0.034−0.665 mol/kg), as previously described.[6] NMR tubes (5 mm) were loaded and sealed off under an inert argon atmosphere.

^{19}F diffusion measurements were performed on a Bruker ACP-250 spectrometer with an HR-50 high-resolution VT diffusion probe for 5 mm samples (Cryomagnet Systems Inc., Indianapolis, IN), using the Hahn echo pulse sequence.[11] Gradient pulses were generated by a home-built gradient unit driven by a Kenwood PD35-20D power supply.

The gradient pulses, of rectangular shape with duration δ and strength g, were applied on each side of the phase-inverting 180° pulse with a separation of $\Delta = \tau$. In addition, three gradient pulses were applied prior to the pulse sequence in order to obtain a steady-state eddy-current condition.[12] The relaxation delay between experiments was more than 5 times the longitudinal relaxation time T_1. The attenuation of the spin echo, $S(2\tau)$, is described by eq 1,[13] where γ is the magnetogyric ratio and T_2 is the transverse relaxation time.

$$S(2\tau) = S(0)e^{-(\gamma g\delta)^2 D(\Delta-\delta/3)}e^{-2\tau/T_2} \qquad (1)$$

The diffusion experiments were performed by varying δ while keeping the other parameters constant. Thus, the second exponent will not vary during the experiments and can be incorporated into $S(0)$. The experimental parameters were $\tau = \Delta = 100$ ms, $\delta = 1-20$ ms, and $g = 29.0-48.1$ Gauss/cm. The temperature distribution in the sample was carefully controlled to within 2 °C by a heated air stream passing over the sample. Measurements were performed at $T = 56$ and 97 °C, respectively. From excellent fits to eq 1, and the absence of characteristic phase twists in the signal that would indicate correlated flow, we conclude that our data reflect diffusive motion and that any contribution from thermal convection is negligible for all concentrations and temperatures investigated.

Results and Discussion

Figure 1 shows the resulting diffusion coefficients for ionic species containing ^{19}F nuclei as a function of salt concentration along with equivalent conductivity and viscosity data, calculated from VTF fits reported in ref

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Table 1

O:Li	conc (mol/kg)	$T = 56$ °C			$T = 97$ °C		
		$D(^{19}F)$ (10^{-8} cm^2/s)	η^a (P)	$D(^{19}F) \times \eta$ [10^{-8}(P cm^2)/s]	$D(^{19}F)$ (10^{-8} cm^2/s)	η^a (P)	$D(^{19}F) \times \eta$ [10^{-8}(P cm^2)/s]
495	0.0344	6.78	2.99	20.3			
295	0.0576	6.51	3.15	20.5			
200	0.0846	4.71	3.35	15.8	26.8	1.28	34.2
98.2	0.170	4.15	4.08	16.9			
65.9	0.250	3.73	4.93	18.4	17.4	1.61	27.9
23.1	0.665	1.28	13.65	17.5	9.3	2.97	27.6

[a] From ref 4; values at 97 °C have been extrapolated from reported VTF fits.

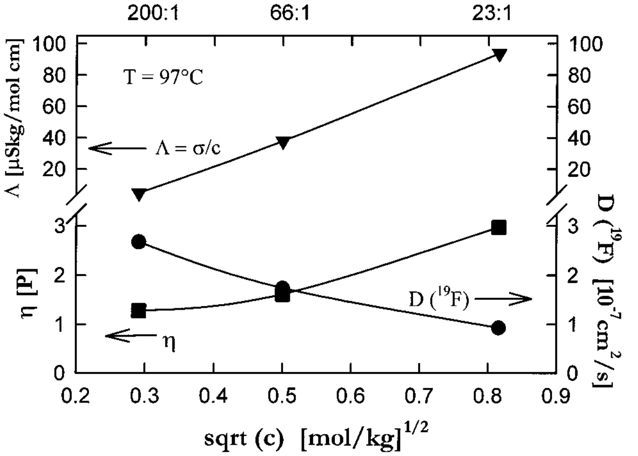

Figure 1. Molar conductivity, viscosity, and diffusion coefficients for anionic species as a function of concentration at 97 °C. Conductivity and viscosity data have been calculated from VTF fits reported in ref 4.

4. The increasing trend of Λ with increasing salt concentration is not observed for the ^{19}F diffusion coefficients. Rather, the $D(^{19}F)$'s decrease monotonically with increasing salt concentration. Table 1 summarizes diffusion coefficients and viscosity data[4] over a range of concentrations and temperatures. According to Table 1, a Stokes–Einstein relationship (*i.e.*, $D \sim 1/\eta$) exists between the ^{19}F diffusion coefficients and the electrolyte viscosity over a large concentration range.

Ionic diffusion coefficients may approximately be related to ionic conductivity for dilute binary salt electrolytes through the Nernst–Einstein relation:

$$\Lambda(T) = \frac{F^2}{RT}(D_+ + D_-) \tag{2}$$

where F is Faraday's constant and D_+ and D_- are the cationic and anionic diffusion coefficients, respectively. The principal requirement for this relation to hold is that the ionic entities involved in diffusional motion are the same as those responsible for conduction. Thus, in a dilute solution, information on both the cationic and anionic diffusion coefficients enables one to calculate an "ideal" conductivity, *i.e.*, in the absence of cooperative motion of oppositely charged ions and neutral aggregates. It is, however, generally agreed that anions typically are more mobile than solvated cations in polyether–salt systems,[14,15] and it is therefore clear from the concentration dependence of the anionic diffusion coefficients shown in Figure 1 and Table 1 that the Nernst–Einstein relation does not adequately relate the equivalent ionic conductivity to the present ^{19}F diffusion coefficients. For instance, at 56 °C the $D(^{19}F)$'s *decrease* by a factor of ~5 while Λ *increases* by a factor of ~15 over the O:Li range 495:1 to 23:1.[4]

We note that diffusive motion probed in the pfg-NMR experiment occurs under time scales in the millisecond range, while reported ionic conductivities correspond to DC conditions. Interestingly, restricted diffusion measurements reported by one of us for the analogue endo-methylated system[8] show a fair correlation between the concentration dependence of Λ and the differential salt diffusion coefficient of the electrolyte, which is related to average bulk salt motion over long time scales. Diffusometric experiments probing longer timescales thus seem to better reflect the concentration dependence of the ionic conductivity in these systems.

It is well established that ionic conductivity in macromolecular electrolytes in general does not follow Walden's rule (*i.e.*, $\Lambda \sim 1/\eta$).[16] The diffusivity of globular entities dispersed in a liquid-like solvent is, however, expected to scale inversely with solution viscosity. In view of the microscopic phase separation reported by Prud'homme and co-workers,[9,10] it seems reasonable to attribute the distinctly different concentration dependencies of these ionic transport properties to this phase-segregated morphology. We suggest that pfg-NMR diffusion experiments, probing relatively short time scales, reflect diffusive motion of salt-rich microdomains, while concentration dependencies of transport properties such as ionic dc conductivity and differential salt diffusion coefficients may be influenced by connectivity effects in the system. These issues will be discussed further in a forthcoming publication.[17]

Concluding Remarks

The present study shows that the anionic diffusion coefficient is inversely proportional to solution viscosity in the PPG4000–$LiCF_3SO_3$ electrolyte system over a large concentration range, as probed by ^{19}F pfg-NMR spectroscopy. This is in contrast to the behavior of the equivalent ionic conductivity which generally exhibits a rapid increase with increasing concentration over the same range in PPG4000-based electrolytes.[4] We suggest that these differences are attributable to the microphase separation previously reported for these systems[9,10] and to differences in the timescales probed with the different experimental techniques.

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References and Notes

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