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Ionic Mobility in Macromolecular Electrolytes: The Failure of Walden's Rule

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In macromolecular electrolytes, both in solid, entangled polymers and in liquid oligomeric systems, the ionic mobility appears to be determined primarily by the fractional free volume. Ionic mobility does not vary inversely with the viscosity of the electrolyte, as predicted by Walden's rule. For unentangled poly(ethylene glycol)/poly(ethylene oxide) blend electrolytes in the melt at constant $CoBr_2$ concentration, the ionic mobility can be simply related to the free-volume dependent friction coefficient ζ. The viscosity has a greater dependence on molecular weight than does the ionic mobility. In liquid oligomeric $CoBr_2$-PEG systems, the viscosity increases linearly with salt concentration at constant free volume. These results lead to the following proposed expression for ionic mobility: $\mu \propto c/\Delta\eta$. This expression is consistent with data for $CoBr_2$–polyether systems in which the numbers of charged species were determined independently by UV–visible spectroscopy.

Introduction

Understanding ionic transport through macromolecular media remains a central goal in the field of solid polymeric electrolytes.[1-4] For many conventional electrolytes, the ionic mobility is approximately inversely proportional to the solution's macroscopic viscosity. This relationship, first suggested by Walden,[5] is extremely useful because it relates microscopic ionic behavior to an easily measured macroscopic property of the system. It is obvious that "Walden's rule" is inappropriate for solid polymeric electrolytes which often have significant ionic conductivities despite their effectively infinite viscosities. Instead, various theories including free volume theory[6-8] and dynamic percolation theory,[1,9] have been used to model the ionic conduction mechanism in these systems. Though these polymer electrolytes are macroscopically solid, their glass transition temperatures are typically very low, and ionic transport is facilitated by the considerable segmental motion of the polymer.

A somewhat more subtle issue concerns ionic mobility in unentangled, oligomeric melts. Liquid oligomeric electrolytes are commonly employed[10-15] in fundamental studies, mainly because liquids are often simpler to investigate experimentally. Investigations of ionic conductivity in oligomeric electrolytes[16,17] indicate that Walden's relationship does not seem to hold for these systems, in spite of their liquid nature. In particular, it has been noted that the "Walden product", $\Lambda\eta$, increases with salt concentration in these systems[18,19] though this trend is not expected from Walden's rule. These anomalies have not been adequately clarified; moreover, the presumption of the validity of Walden's rule may lead to erroneous conclusions, such as in a recent study of triflate salts in oligomeric poly(propylene glycol)[20] in which Walden's rule was used to evaluate the extent of salt dissociation without a prior determination that Walden's rule is appropriate for such systems.

This study addresses ionic mobility in liquid, oligomeric systems. It shows that Walden's simple relationship between ionic mobility and viscosity is no more appropriate for oligomeric systems than it is for entangled solid polymeric electrolytes and that it should not be used to calculate the fractional salt dissociation in these systems. Instead, it appears that the ionic mobility in both entangled and unentangled macromolecular systems is determined primarily by free-volume considerations. The viscosity of a macromolecular system is an unreliable indicator of fractional free volume and thus of ionic mobility as well.

Experimental Procedures

Poly(ethylene glycol) (PEG, viscous liquid, M_{av} 400, Polysciences), poly(ethylene oxide) (PEO, solid, M_{av} 7500, Polysciences), poly(tetramethylene glycol) (PTMG, viscous liquid,

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M_{av} 650, Scientific Polymer Products), and the nominally anhydrous salts $CoBr_2$, $CdBr_2$, $CaBr_2$ (Alfa/Johnson Matthey), and $ZnBr_2$ (Cerac) were used as received.

The electrolyte solutions were prepared mainly by using ethanol as an intermediate solvent which was ultimately driven off under reduced pressure, as discussed earlier.[15] All solutions were dried for at least 24 h at 100–110 °C in a vacuum oven prior to measurement. In all cases, the moisture content, as determined by Karl Fischer titration, was in the range 100–400 ppm by weight, corresponding to a molar ratio of salt to water generally in excess of 50.

Ac impedance analysis, as discussed by Bruce,[21] was used to determine the bulk conductivities of the electrolyte solutions in a Teflon cell with blocking platinum electrodes. Measurements were made over the frequency range of 10^2–10^6 Hz. Temperature was maintained within ±0.5 °C.

Solution viscosities were measured using an Irvine-Park falling needle viscometer. Temperature was controlled with a water bath to within ±0.3 °C. Measurements were taken at two shear rates for each sample within the range 2–40/s. All solutions were Newtonian (independent of shear rate within 3%).

Thermal analysis was carried out using a Du Pont 910 differential scanning calorimeter. The samples were analyzed from −100 to 40 °C at a scan rate of 10 °C/min. The glass transition temperature was defined as the linear extrapolation of the transition to the baseline. Since PEG crystallizes quickly, the samples were rapidly quenched from room temperature with liquid nitrogen to ensure that they were completely amorphous at the start of each experiment. Any crystallization of the PEG would cause a higher effective concentration of salt in the amorphous phase and thus a higher value of T_g would be measured. To verify that the samples were in fact amorphous at the start of the DSC experiment, the areas under the exothermic cold crystallization peak (around −24 °C) and the endothermic melting peak (around 9 °C) were measured and found to be approximately equal.

Background

In 1906, Walden[5] proposed that the product of the limiting electrolytic conductance Λ_0 and the viscosity of the pure solvent η_0 is a constant for all temperatures and solvents for a given electrolyte. It can be said that a system follows Walden's rule if an inverse relationship between ionic mobility and viscosity holds. This empirical rule is fairly reliable for large organic ions in various single solvents.[22]

The ionic conductivity of an electrolyte, σ, can be expressed generally as

$$\sigma = \sum n_i q_i \mu_i \qquad (1)$$

where n_i = the number density of charge carriers of species i, q_i = the charge on species i, and μ_i = mobility of species i. If the mobilities of all charged species are approximately the same, then

$$\sigma \propto ac\mu \qquad (2)$$

where a = the fractional salt dissociation (a function of temperature, concentration, and solvent) and c = the salt concentration. If Walden's rule ($\mu \propto 1/\eta$) is valid then

$$\Lambda\eta \propto a \qquad (3)$$

where Λ = the equivalent conductance ($=\sigma/c$) and η = the viscosity of the solution.

Studying the dependence of the Walden product $\Lambda\eta$ on solvent, concentration, and temperature can be very helpful in learning about ion dissociation in many systems.[23,24] However, $\Lambda\eta$ is not a good indicator of ion dissociation in macromolecular media. In these systems, the macroscopic viscosity is generally much higher than the local viscosity experienced by the ions.[25,26] This is clearly evident for solid, entangled polymers and, in fact, has been observed as early as 1945 by Mead and Fuoss.[27] But even in various studies of liquid oligomeric electrolytes, several researchers have found deviations from Walden's rule. In these systems, $\Lambda\eta$ generally increases with molecular weight and salt concentration, an effect not explained realistically with Walden's rule.

One reason for the confusion regarding ionic mobility in macromolecular electrolytes has been the assumption[20] that the macroscopic viscosity of a macromolecular system is a good measure of its local "microscopic" viscosity, as long as chain entanglements are absent. Hence, while it is obvious that the macroscopic viscosity is decoupled from the segmental mobility in high molecular weight PEO-based solid electrolytes, it has been thought that the viscosity should correlate well with ionic mobility for liquid oligomer systems in which the molecular weight is below the point at which chain entanglements develop. In truth, the ionic mobility will not be correlated to the macroscopic viscosity of the solution unless the ions are tightly bound to the macromolecules; in such cases the ionic motion is linked to the large-scale motion of the macromolecular chains. This situation is most probable for small, multivalent cations. For example, Shi and Vincent[28] recently showed that the mobility of the Mg(II) ion in polyether media changes dramatically at the onset of entanglement: below the entanglement molecular weight, Mg(II) moves by dragging a chain with it; above it, Mg(II) is not mobile. In general though, the transport behavior of macromolecular electrolytes should not change abruptly at the chain-entanglement molecular weight. Unless tight ion-binding is predominant, the ionic mobility is determined not by the long-range diffusion of the macromolecular solvent but instead by the local relaxation modes of the macromolecular host.

For linear high molecular weight polymers, it has been verified experimentally that the zero-shear melt viscosity is proportional to $M^{3.4}$, where M is the molecular weight. But even for short-chain oligomers, in which chain entanglements are absent, the melt viscosity is strongly dependent on the molecular weight. In fact, for short linear macromolecules, the viscosity, η, is proportional to M at constant free volume.[29,30] More generally, for unentangled macromolecules, the viscosity can be modeled as

$$\eta \propto M\zeta \qquad (4)$$

where ζ is the friction coefficient per monomer unit. Theoretical justification for this relation has been presented by Ferry,[31] and it has been experimentally verified in many studies.[29,32-34]

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The friction coefficient, ζ, can be thought of as the "microscopic" viscosity experienced by the chain segments. Determined primarily by the free volume, it is dependent on both the molecular weight and the temperature. For low molecular weights, ζ increases with M_n, because of the free volume associated with end groups, but eventually reaches a limiting value ζ_0. The temperature dependence of ζ follows Williams-Landel-Ferry (WLF) behavior.[35] Berry and Fox[30] and Ferry[31] have discussed the friction coefficient in detail.

The ions in macromolecular media should encounter a frictional resistance closely related to that experienced by the polymer segments themselves in their random thermal motions. In macromolecular electrolytes, then, the ionic mobility cannot be simply proportional to η^{-1}, since the viscosity is determined to a large degree by the molecular weight of the system. This leads us to suggest that the ionic mobility, μ, varies as $1/\zeta$ for these systems. This proposal is consistent with Ferry's discussion[31,36] of the correlation of the friction coefficient with the diffusion of small neutral molecules in polymers, for the condition $T - Tg > 40°$. Indeed, Scheirer and Dannhauser[37] have already highlighted the importance of the friction coefficient in determining ion mobility for salts dissolved in polystyrene-diphenylmethane mixed solvents.

Results and Discussion

$CoBr_2$-PEG/PEO Blends. To test the validity of the proposed relation between μ and ζ for oligomeric melts, a series of electrolyte solutions formed with blends of poly(ethylene oxide) of two different molecular weights were investigated. In these systems, the average molecular weight was varied in a controlled way, so that the dependence of the viscosity and ionic mobility on average molecular weight could be explored.

The electrolytes studied consisted of $CoBr_2$ dissolved in various PEG/PEO blends. Note that poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) have the same repeat unit, (CH_2CH_2O), the term "glycol" simply indicating low molecular weight. For this study, PEG of average molecular weight 400 and PEO of average molecular weight 7500 were used; the former is a viscous liquid (η at 25 °C = 95.9 cP, $T_m \approx 0$ °C), the latter a white, waxy solid ($T_m \approx 60$ °C). Blends containing 3.5-50 wt % PEO were prepared. Although the critical molecular weight M_c for entanglement coupling is 4400 for poly(ethylene oxide),[31] the value of M_c increases when a polymer is diluted with a low molecular weight oligomer or solvent.[38] A simple calculation based on previously proposed laws for entanglement in diluted systems of this type[39,40] indicates that all blends studied here are unentangled, in the regime where $\eta = M\zeta$ is valid.

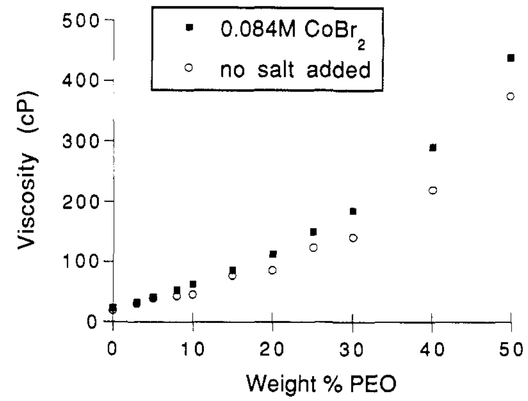

Figure 1. Viscosities of PEG/PEO blends at 70 °C versus weight percent PEO, with and without added $CoBr_2$.

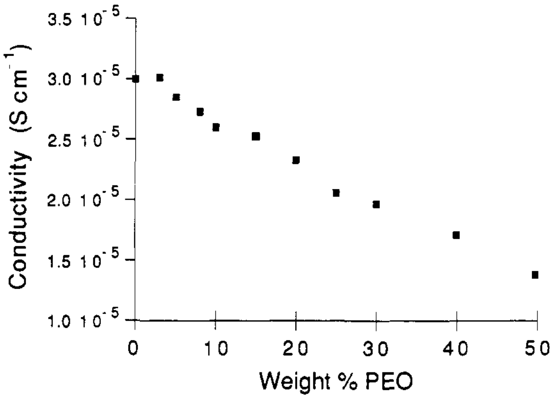

Figure 2. Conductivities of PEG/PEO blends with 0.084 M $CoBr_2$ at 70 °C versus composition of the blend.

Since all of the blends with PEO were waxy solids at room temperature, all measurements were made at 70 °C, above the melting point of the materials. Electrolyte systems were prepared by adding $CoBr_2$ to each of the blends such that the salt concentration was 0.084 M (±0.005 M) in each case, a concentration relatively low for studies of polyether-salt systems. Because PEG and PEO are so similar chemically, it has been assumed that the concentrations and types of neutral and charged species present were the same for each blend, since the overall salt concentration was the same in each case. At this concentration, the effect of the added salt on the viscosity is not too great. The viscosities of the blends, with and without added salt, as a function of weight percent PEO, are shown in Figure 1. All systems exhibited Newtonian behavior, confirming the absence of entanglements. The conductivities of the electrolytes are shown in Figure 2.

If the proposed hypothesis about ionic mobility is correct, then $\mu \propto 1/\zeta$. From eqs 2 and 4

$$\Lambda\eta \propto aM \qquad (5)$$

Assuming that the salt dissociation parameter a is the same for all the electrolyte blends, a plot of $\Lambda\eta$ versus M should be linear. As discussed by Allen and Fox,[29] the proper molecular weight to use for M is the weight average molecular weight M_w. Note that in these blends, M_w is proportional to the weight percent PEO since by definition, $M_w = \sum w_i M_i$, where w_i is the weight fraction of chains of molecular weight M_i. The product $\Lambda\eta$ versus weight percent PEO is presented in Figure 3; the plot is indeed linear, giving strong support for the hypothesis that the parameter controlling the ionic mobility is the friction coefficient. If Walden's rule had been valid here, the product $\Lambda\eta$ would have had no dependence on the blend composition.

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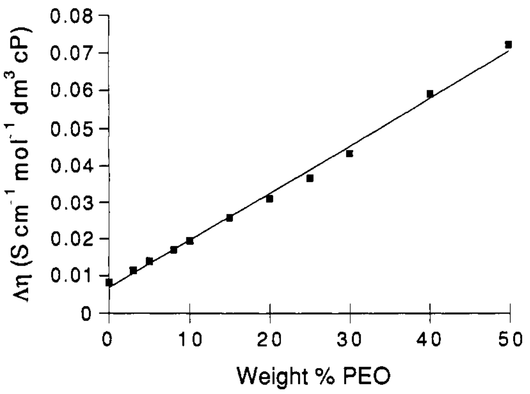

Figure 3. Product $\Lambda\eta$ as a function of blend composition for 0.084 M $CoBr_2$–PEG/PEO.

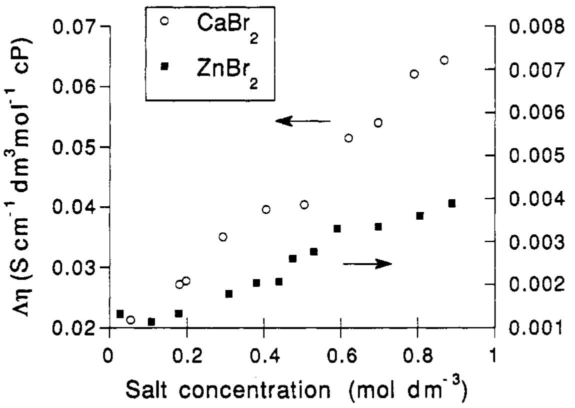

Figure 4. Product $\Lambda\eta$ versus concentration for $CaBr_2$–PEG and $ZnBr_2$–PEG.

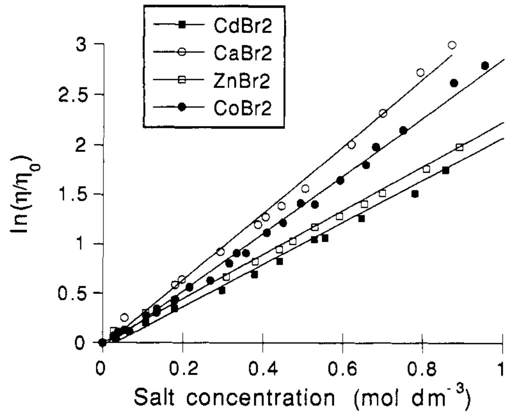

Figure 5. ln (η/η_0) versus salt concentration for MBr_2–PEG systems.

MBr_2–PEG Systems. Walden's rule also proves to be invalid for oligomeric electrolytes as the salt concentration alone is varied. One might have expected Walden's rule to hold for these liquid systems since the molecular weight of the solvent is unchanging and since the macroscopic viscosity is determined at least in part by the system's fractional free volume. However, the viscosity is influenced by other effects as well.

In a preliminary study[41] of the characteristics of several divalent metal salt/PEG systems, the room-temperature conductivities and absolute viscosities for MBr_2–PEG (M = Ca, Co, Zn, and Cd) were studied as a function of salt concentration. Figure 4 presents the modified Walden product $\Lambda\eta$ ($=\sigma\eta/c$) as a function of salt concentration for two MBr_2–PEG electrolytes. It is clear that $\Lambda\eta$ increases with concentration for $CaBr_2$–PEG and $ZnBr_2$–PEG. The $CoBr_2$–PEG and $CdBr_2$–PEG systems behave similarly. If Walden's rule were used (eq 3), it would appear that the number of charge carriers per mole of added salt increases with salt concentration, a strange result considering that ion association and aggregation are generally more pronounced at higher salt concentrations. Indeed, several Raman studies of $NaCF_3SO_3$ in PEG and PPG[42–44] indicate that the number of free ions decreases with increasing salt content. Therefore, it is not reasonable that a increases monotonically with concentration for all the MBr_2–PEG systems. Thus it is apparent that the ionic mobility is not simply related to the bulk viscosity in these systems, which is to say that Walden's rule is not valid, though for reasons less obvious than the effect of molecular weight.

It is clear that, in all four PEG electrolytes, the viscosity increases exponentially with salt content, such that $\eta = \eta_0 e^{bc}$, where η_0 = viscosity of pure PEG, b = a constant, and c = salt concentration. Figure 5 shows a plot of ln (η/η_0) vs c for the MBr_2–PEG electrolytes; the linearity is very good in all four cases and b = 3.39, 2.93, 2.24, and 2.15 dm^3/mol for M = Ca, Co, Zn, and Cd, respectively. Albinsson et al.[20] noted similar behavior for alkali metal triflate–PPG systems and cited Doolittle's expression[45] for the temperature dependence of a liquid's viscosity:

$$\eta = Ae^{B/f} \tag{6}$$

where A and B are constants for a given substance, and f is the fractional free volume (dependent on temperature). The molecular weight of the system is reflected in the preexponent A, while the temperature-dependent term, B/f, is almost independent of the molecular weight. To explain their experimental data, Albinsson et al. proposed that $f \propto 1/c$ for their systems. If this were true, and the viscosity determined solely by the changes in fractional free volume, then Walden's rule should be valid for these systems.

The fractional free volume f is defined[46] as

$$f = f_g + (T - T_g)\alpha_f \tag{7}$$

where f_g = the fractional free volume at and below T_g, and α_f is the thermal expansion coefficient of the free volume. Assuming that α_f does not vary much as salt is added to the polyether solvent, f is proportional to $(T - T_g)$. Using DSC, we have measured the onset of the glass transition temperature for $CoBr_2$–PEG as a function of salt concentration (Figure 6). As expected, T_g increases with salt content. A plot of $(T - T_g)$ versus $1/c$ is shown in Figure 7; the curve is clearly nonlinear, in definite contrast to the proposal of Albinsson et al. that $f \propto 1/c$. This result signifies that viscosity is not a simple indicator of free volume.

To clarify the importance of free volume in determining viscosity, the viscosities of several $CoBr_2$–PEG electrolytes were measured at temperatures such that $(T - T_g)$ is constant, an effective iso-free volume state. The viscosities

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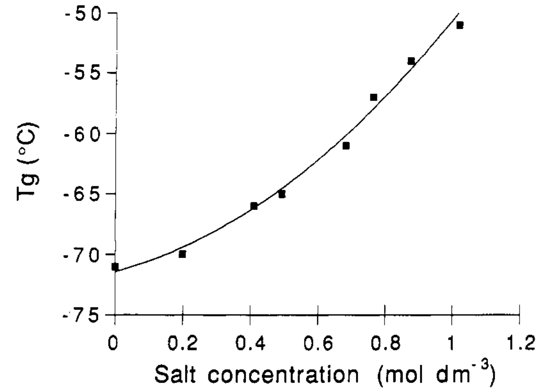

Figure 6. Variation of the glass transition temperature with salt content in $CoBr_2$–PEG systems. The solid line is given as a guide to the eye.

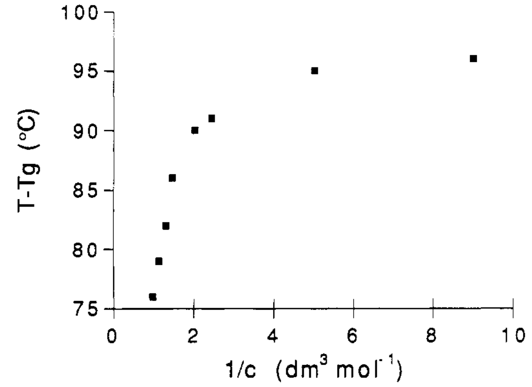

Figure 7. Variation of (T − T_g) with the inverse of salt concentration for $CoBr_2$–PEG.

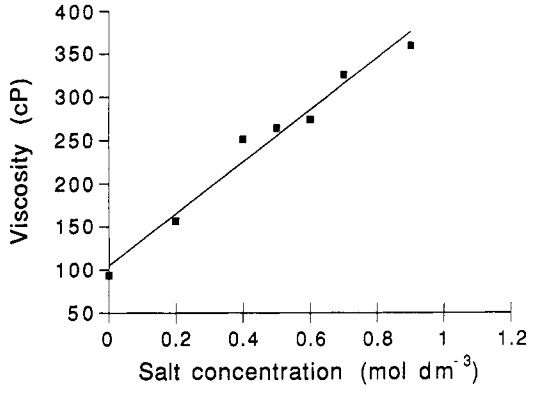

Figure 8. Variation of the "iso-free-volume" viscosity with salt content for $CoBr_2$–PEG. All viscosities were measured at $T - T_g$ = 96 °C.

of $CoBr_2$–PEG at $T - T_g$ = 96 °C as a function of salt concentration are shown in Figure 8.

The WLF equation[35] is known to accurately model the viscosities of macromolecules:

$$\log \frac{\eta(T)}{\eta(T_s)} = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)} \tag{8}$$

where $\eta(T_s)$ is the viscosity at some reference temperature T_s and C_1 and C_2 are constants. Since T_g can be chosen as T_s, the condition $T - T_g$ = constant should imply constant viscosity (we assume that C_1 and C_2 do not vary as salt is added to the system). Instead, the "iso-free-volume viscosity" increases linearly with salt content (Figure 8). From this result, it is clear that the viscosity of polyether–salt systems is not determined solely by free volume considerations. Indeed, if the viscosity were determined entirely by the free volume, Walden's rule should be valid.

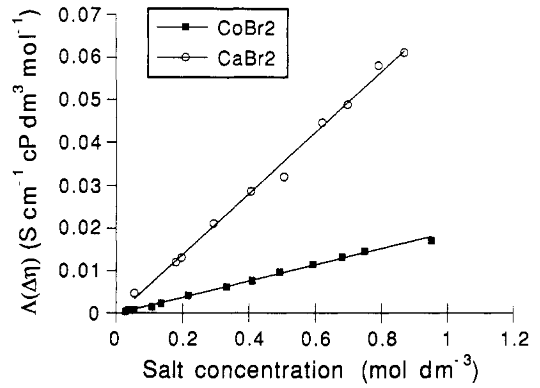

Figure 9. Variation of the product $\Lambda(\Delta\eta)$ versus salt concentration for $CaBr_2$–PEG and $CoBr_2$–PEG.

Unfortunately, we can only speculate on the reason for the linear rise of the iso-free volume viscosity with salt content. This behavior is certainly reminiscent of Einstein's suggestion[47] that the viscosity of a colloidal suspension will increase linearly with the volume fraction of dispersed particles; however, our solutions are seemingly single phase. This trend in viscosity is more likely due to the interaction of the salt with the polyether molecules. A polyether complexing a cation will find its ability to flow past its neighbors much reduced; the associated cation not only makes the polyether bulkier but it also decreases its flexibility. This would be reflected in an increased macroscopic viscosity. Physical cation-induced cross-linking of polyether chains would also increase the system's viscosity at constant free volume, since higher molecular weight species would be generated.

In any case, we propose that the ionic mobility in salt–polyether systems is determined solely by the changes in the free volume of the system. This is consistent with the findings of Le Nest et al.[7,8] for PEO-based network electrolytes with alkali metal salts. Hence, if the macroscopic viscosity is to be used as a probe of the ionic mobility μ in MBr_2–PEG systems, the additional linear dependence on salt concentration seen in Figure 8 must be corrected. Therefore, for these systems, we suggest

$$\mu \propto c/\Delta\eta \tag{9}$$

where $\Delta\eta$ is $\eta - \eta_0$, the change in the system's viscosity brought about at the salt concentration c. The denominator is chosen to be $\Delta\eta$ rather than η to prevent artificially forcing the ionic mobility to zero as the salt concentration approaches zero.

This empirical relation results in more reasonable conclusions about the MBr_2–PEG electrolytes. Substituting our expression into eq 3, we arrive at

$$\Lambda(\Delta\eta) \propto ac \tag{10}$$

Plots of $\Lambda(\Delta\eta)$ vs c for two MBr_2–PEG systems are given in Figure 9. The much higher values of $\Lambda(\Delta\eta)$ for $CaBr_2$ than for $CoBr_2$ can be attributed to the higher fraction of salt dissociation expected in $CaBr_2$–PEG, as discussed previously.[41] The linearity in Figure 9 is very good for both cases, and linear plots are found for M = Zn and Cd as well. From this, we conclude that the salt dissociation parameter a is relatively constant as the salt content is

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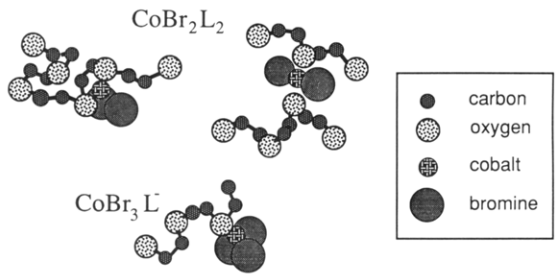

Figure 10. Graphical illustration of two of the possible species in $CoBr_2$–PEG. For complexes, L = ligand (an ether oxygen in this case). Both intramolecular (left) and intermolecular (right) coordination are shown for $CoBr_2L_2$.

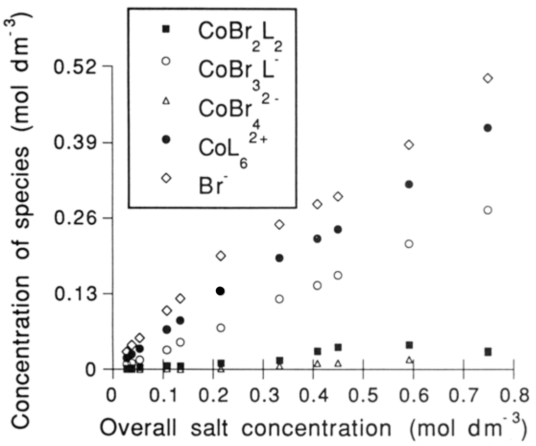

Figure 11. Concentrations of complex species determined by UV–visible spectroscopy as a function of overall salt content for $CoBr_2$–PEG.

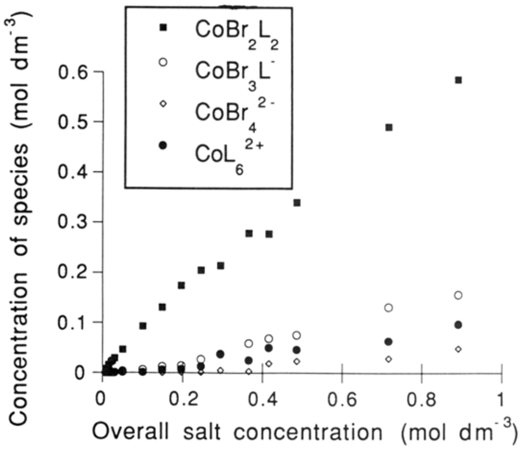

Figure 12. Concentrations of complex species determined by UV–visible spectroscopy as a function of overall salt content for $CoBr_2$–PTMG. The concentrations of free Br^-, not shown, are negligible.

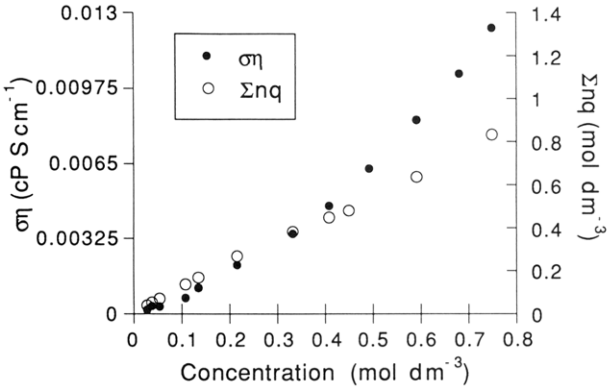

Figure 13. Product $\sigma\eta$ and the experimentally determined $\sum nq$ versus salt concentration for $CoBr_2$–PEG.

varied, a more realistic result. This does not imply that there is complete dissociation, only that the fraction of salt dissociated remains roughly constant. These results are consistent with those of Le Nest and Gandini[8] for several PEO-based networks with $LiClO_4$ salt; they found the conductivity to be proportional to salt concentration at constant free volume.

UV–Visible Spectroscopic Studies. Further studies were carried out to test the hypothesis posed in eq 10 more rigorously with electrolytes whose concentrations of charge carriers ($\sum nq$) have been determined independently using UV–visible spectroscopy.

The systems investigated were $CoBr_2$–PEG and $CoBr_2$–PTMG. PTMG is poly(tetramethylene glycol), M_{av} 650, with the repeat unit ($CH_2CH_2CH_2CH_2O$). An earlier study[15] showed that the types of species found in $CoBr_2$–polyether systems are analogous to those in $CoBr_2$–acetone systems. The typical complexes are ${}^{oct}CoL_6^{2+}$, ${}^{oct}CoBrL_5^+$, ${}^{tet}CoBr_2L_2$, ${}^{tet}CoBr_3L^-$, and ${}^{tet}CoBr_4^{2-}$, where L is a ligand atom (in these cases either an acetone molecule or an ether oxygen from a polyether), and the left superscript indicates octahedral or tetrahedral geometry. For clarification, a graphical representation of two of these species in poly(ethylene glycol) systems is given in Figure 10.

The isolated visible spectra of the individual tetrahedral cobalt complexes were determined earlier[15] and allow a quantitative determination of the concentration of these species. The intensities of the octahedral complexes were too low to differentiate between CoL_6^{2+} and $CoBrL_5^+$ and the predominant octahedral species was assumed to be CoL_6^{2+}. The concentrations of octahedral species and of free Br^- were calculated by subtraction. The calculated concentrations of the various complexes for $CoBr_2$–PEG and for $CoBr_2$–PTMG as a function of overall salt content are shown in Figures 11 and 12. For PEG, the predominant species are Br^- and CoL_6^{2+}, and the neutral $CoBr_2L_2$ species are negligible. For PTMG, in contrast, neutral species predominate, although charged species such as $CoBr_3L^-$ do appear at higher overall $CoBr_2$ concentrations. These differences can be explained in terms of the chelate effect.[15]

From the UV–visible spectroscopic results, the total number of charge carriers as a function of salt concentration can be calculated. Clearly $CoBr_2L_2$ is a neutral species and will not contribute to charge transport. Furthermore, the octahedral species CoL_6^{2+} is not expected to be very mobile because of its strong interactions with the polyether molecules. Therefore $\sum nq$ was taken as $[Br^-] + [CoBr_3L^-] + 2[CoBr_4^{2-}]$ where $[x]$ indicates the concentration of species x.

Using this quantitative assessment of $\sum nq$ as a function of overall salt content for the $CoBr_2$–PEG and $CoBr_2$–PTMG systems, the validity of the previously discussed models can be checked. From eq 1, Walden's rule implies

$$\sigma\eta \propto \sum nq \qquad (11)$$

Data regarding the conductance and viscosity of $CoBr_2$–PTMG were reported previously.[15] In Figures 13 and 14, $\sigma\eta$ and $\sum nq$ versus salt concentration are plotted for $CoBr_2$–PEG and $CoBr_2$–PTMG. Since the proportionality constant for eq 11 is unknown, the plots were scaled such that agreement was achieved for $\sigma\eta$ and $\sum nq$ at low concentrations. However, for both polyether systems, there are great deviations at higher concentrations. The continuing

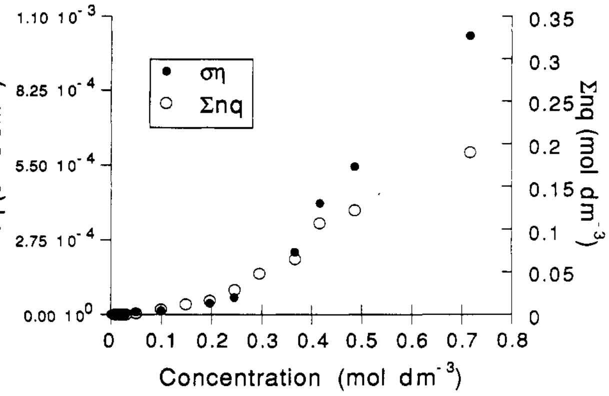

Figure 14. Product $\sigma\eta$ and the experimentally determined $\sum nq$ versus salt concentration for $CoBr_2$–PTMG.

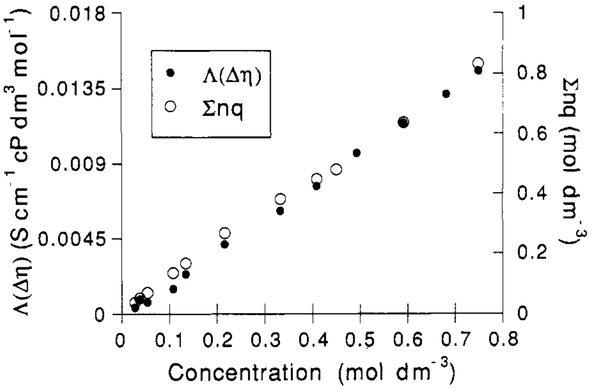

Figure 15. Function $\Lambda(\Delta\eta)$ and the experimentally determined $\sum nq$ versus salt concentration for $CoBr_2$–PEG.

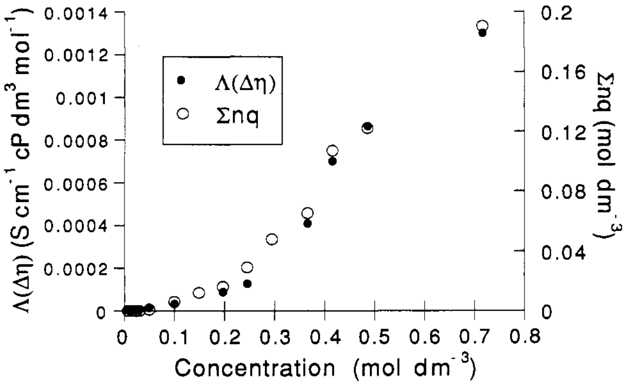

Figure 16. Function $\Lambda(\Delta\eta)$ and the experimentally determined $\sum nq$ versus salt concentration for $CoBr_2$–PTMG.

upward curvature of $\sigma\eta$ is not reflected in the experimentally determined values of $\sum nq$. As expected from the earlier discussions, Walden's rule fails for these systems.

The previous discussion of macromolecular electrolytes predicts that $\Lambda(\Delta\eta) \propto \sum nq$ (from eq 10). Plots of $\Lambda(\Delta\eta)$ and $\sum nq$ versus c for the two systems, scaled to achieve maximum correspondence, are given in Figures 15 and 16. The agreement is now excellent for both systems, demonstrating consistency between our hypothesis (given in eq 10) and the experimental results.

Note that $\sum nq$ for $CoBr_2$–PTMG exhibits very nonlinear behavior as a function of salt concentration. This is because the system consists of predominantly neutral $CoBr_2L_2$ species. The $CoBr_3L^-$ species which are apparently responsible for the bulk of the ionic transport achieve significant concentrations only at higher overall salt contents when the formation of such bromo complexes is more favored. That the function $\Lambda(\Delta\eta)$ so closely models $\sum nq$ for this exceptional system lends strong support to our discussions.

Conclusions

For macromolecular electrolytes, the ionic mobility μ is not simply inversely related to the viscosity η, as predicted from Walden's rule. This conclusion is of course blatantly obvious for solid polymeric electrolytes which can possess high ionic conductivities despite their solid nature. However, for electrolytes involving unentangled oligomeric melts or dilute polymer solutions, this issue has not been adequately clarified until now.

Since the viscosity of a macromolecular system is largely determined by its molecular weight, a more suitable parameter for modeling the ionic mobility μ in macromolecular electrolytes is the free-volume-dependent friction coefficient ζ. We have proposed that μ is inversely proportional to ζ at temperatures much higher than the glass transition temperature. This is consistent with observations that the diffusion of neutral molecules in polymers is linked to the polymer's friction coefficient.[31] Our experimental results for PEG/PEO blends are modeled well by this relationship.

Indeed, this hypothesis suitably explains several "anomalies" reported in the literature. For example, in polyether–salt electrolytes, as the molecular weight of the polyether increases, the ionic conductivity is not altered much despite dramatic increases in the viscosity of the system.[2,16] For systems involving mixtures of macromolecules and low molecular weight species, the "decoupling" of viscosity and ionic mobility has also been reported.[17,26,48] Although many of these investigations pointed out departures from Walden-type behavior, the underlying causes of such deviations were not addressed. From this work, it should be clear that the viscosity largely reflects the average molecular weight of the system, while the ionic mobility is determined only by a local "microviscosity", which can be related to the fractional free volume or to the friction coefficient ζ.

A more important conclusion of this paper is that Walden's rule is inappropriate for macromolecular systems, even when the average molecular weight is not varied. It has been seen in this work, as well as in previous investigations[16,18-20] that for several polyether–salt systems, the modified Walden product $\Lambda\eta$ generally increases with salt concentration, though this is not predicted from Walden's primitive treatment. We believe that this curious phenomenon does not indicate that salt dissociation is more effective at higher salt concentrations, as has been suggested;[20] instead, the trend is more likely due to the inadequacy of the viscosity as a measure of ionic mobility. Indeed, our studies of salt–polyether systems as a function of salt concentration have shown that the viscosity is determined by effects other than free-volume variation. The variation of the viscosity of $CoBr_2$–PEG with salt concentration at iso-free volume has led us to conclude that ionic mobility in these systems is proportional to $c/\Delta\eta$. From this, we have suggested the relationship $\Lambda(\Delta\eta) \propto \sum nq$ (a variation of eq 10). For $CoBr_2$–PEG and $CoBr_2$–PTMG, where $\sum nq$ as a function of overall salt concen-

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tration can be determined independently using UV–visible spectroscopy, the agreement between theory and experiment is excellent.

While our proposed relationship is convenient, its empirical nature must not be overlooked; the parameter $c/\Delta\eta$ is only a good measure of ionic mobility because it happens to model the free volume-dependent parameter ζ well, for our systems. For general cases, the glass transition temperature, rather than the bulk viscosity, will give the most accurate insight into the ionic mobility.

It is also important to note that, if the salt–polyether interactions and the number of charge carriers are unchanged by temperature, the electrolytes will in fact follow Walden's rule as temperature is varied, simply because the viscosity will reflect only changes in free volume in such situations. This ironic coincidence may have compounded the confusion in the field of polymer electrolytes. Indeed, Watanabe et al.[18] did note that $\Lambda\eta$ = constant, as temperature was varied, for $LiClO_4$–PPG systems at any given salt concentration. McLin and Angell[19] and Albinsson et al.[20] also found that $\Lambda \propto 1/\eta$ as temperature was varied for certain of their dilute electrolytes. For cases where $\Lambda\eta$ is dependent on temperature, the charged species or the salt–polyether interactions may be changing with temperature.

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