

Table 2 - Thermodynamic Parameters

I(M)	ΔH (kJ/mol)	ΔS (J/mol K)
0.01	-246	-819
0.02	-251	-839
0.04	-189	-634
0.06	-187	-629
0.10	-105	-363

of the ligand.

The stability constant β_1 follows the same pattern as EW, but the relative ranges of variation are much larger. The decrease of β_1 with increasing ionic strength follows roughly a linear $\log \beta_1$ vs. \sqrt{I} relationship.

Values of the thermodynamic parameters ΔH and ΔS were obtained from the values of β_1 at different temperatures for each value of ionic strength (Table 2). The large negative values for ΔS suggest that complexation is accompanied by an ordering arrangement of the fulvic acid molecule. Besides both $|\Delta H|$ and $|\Delta S|$ decrease markedly with increasing ionic strength, showing that at high ionic strength Cu(II)-H_nFA interactions are much weaker than in conditions found in natural waters. The results also show that the extent of such interactions depends very much on the water temperature in the environmental temperature range.

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CONDUCTIVITY STUDIES OF A NOVEL POLYMER ELECTROLYTE BASED ON EUROPIUM TRIFLUOROMETHANESULPHONATE

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Summary

In this article conductivity results obtained with a new member of the class of polymer electrolytes are presented. The electrolyte, prepared from europium (III) trifluoromethanesulphonate and a poly(ethylene oxide) host polymer, shows ionic conductivity levels comparable with divalent and trivalent systems previously reported.

Introduction

During the last decade a remarkable number of papers have been published describing the preparation and properties of polymer electrolytes based on monovalent cations with several different anions in a variety of host polymers [1]. The most obvious application of these materials, and until recently the principle motivation for the continuing research effort in this field, is in electrochemical power sources. Already several laboratories have produced prototype cells [2-5] and reported very encouraging results.

More recently attention has turned to the investigation of the properties of divalent [6-8] and trivalent [9-12] salts which form complexes with the donor ether oxygen atoms present in the extended macromolecular chains of poly(ethylene oxide), PEO. Preliminary results from studies of these materials suggest that the range of applications may be significantly greater than that of monovalent electrolytes. Devices which have been proposed as possible

applications of these novel materials are electrochromic and thermoelectrochromic displays, low-cost flexible phosphors and metal ion sensors. Clearly there are also theoretical aspects of the ion transport mechanism in the polymeric medium which may be clarified through the study of multivalent polymer electrolytes.

In this article we report the preliminary results of an investigation of the conductivity behaviour of complexes of PEO with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$. The electrolyte compositions studied span the range $10 < x < 106$, where x corresponds to the ratio of ether oxygens to europium ions.

Experimental

The starting materials used in the preparation of the electrolyte films, PEO (Aldrich, MW 5×10^6), and purified $\text{Eu}(\text{CF}_3\text{SO}_3)_3$, prepared by reaction of the europium oxide Fluka, Puriss, $> 99,9\%$) in aqueous suspension with trifluoromethanesulphonic acid (Aldrich, 98 %), were dried under dynamic vacuum at 45°C for approximately one week, and at 180°C for 48 hours respectively. HPLC grade acetonitrile, (Aldrich), was dried by reflux through freshly regenerated 4A molecular sieves [13] before use as solvent in the preparation of films.

These materials were transferred to a high integrity argon filled glove box, operating under low water levels. Polymer and europium salt mixtures were weighed to a precision of 0.0005g and dissolved in a small volume of dry acetonitrile, (≈ 6 wt. %), to form a viscous solution. The solution was stirred during approximately 24 hours and small volumes were transferred to teflon evaporating cups. These cups were placed in an isolated evaporating chamber, located within a preparative glovebox, through which a flow of dry argon gas was circulated by a low flow rate pump. The carrier gas was passed through a short column of molecular sieves to accelerate the preliminary removal of the casting solvent.

The solid flexible films formed by removal of the excess solvent were transferred to a Buchi TO-50 tube oven and the residual solvent was removed by heating to approximately 60°C under vacuum. Finally, the conductivities of the films were measured between two gold electrodes in a constant volume cell-holder located in a Buchi tube oven. This cell-holder,

Figure 1, was designed specifically for use with polymer electrolytes and permits expansion or contraction of the electrolyte film as phase changes occur while maintaining the electrode separation, and therefore the cell constant, invariant. All conductivity measurements were carried out using a Solartron Model 1250 Frequency Response Analyser and a Solartron Model 1286 Electrochemical Interface under the control of a Acer 500+ PC-XT computer. Conductivities were extracted from the complex plane impedance plots using a sophisticated non-linear least squares data processing package [14, 15].

In studies of polymer electrolytes the quality of the agreement between theoretical and experimental complex plane behaviour has been found to depend, to some extent, on the electrolyte composition. Distorted complex impedance plane semi-circles have been reported by other authors [16], Figure 2 reports a typical set of results obtained during the present study.

Results

The variation of electrolyte conductivity with temperature is shown in Figure 3 for the various electrolyte compositions studied. The behaviour observed is typical of a polymer electrolytes containing two phases, those of uncomplexed crystalline PEO and a crystalline complex formed between the host polymer and the added salt. Analysing the results obtained for compositions between $x = 52$ and $x = 106$ it is apparent that a discontinuity occurs in the temperature range of 60 to 65°C , a range in which free PEO in the electrolyte will melt, forming an amorphous phase. In principle one would expect non-linear Arrhenius plots to be registered at higher temperatures, however in practice the degree of curvature depends on a variety of physical features of the system and in the majority of cases this effect is not discernable in the limited temperature ranges studied.

The data obtained for the $x = 10$ and $x = 13$ compositions are more difficult to analyse without recourse to supporting evidence from other techniques.

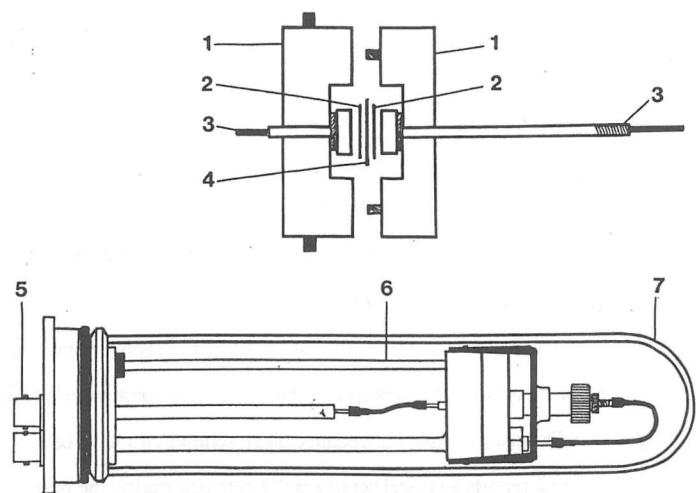


Figure 1. Electrochemical cell-holder : 1 - Macor blocks, 2 - Gold disc electrodes
3 - Current collectors, 4 - Polymer electrolyte film, 5 - BNC connectors,
6 - Temperature probe, 7 - Buchi drying tube.

These compositions show behaviour which may be conveniently modelled by non-linear equations. It is likely that in this composition range the proportion of uncomplexed crystalline PEO present in the electrolyte is very low and so the discontinuity observed in lower concentration ranges is replaced by a slow change of gradient of the logarithm of conductivity versus inverse of temperature graph.

As the proportion of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ increases the conductivity of the electrolyte decreases, a phenomenon often observed in polymer based electrolyte systems and normally ascribed to the effect of the presence of ionic species on the mobility of the polymer chains.

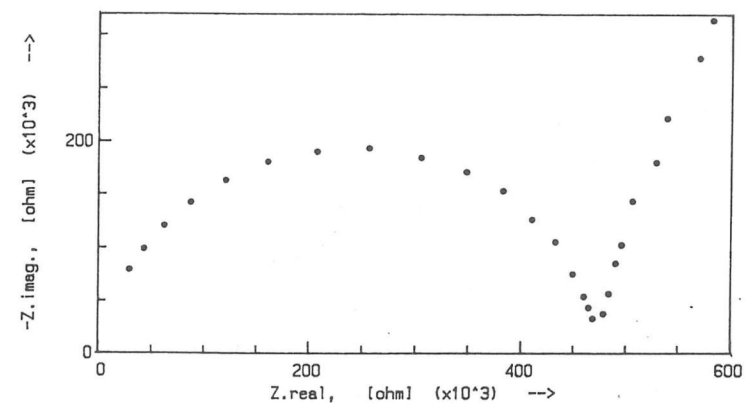


Figure 2. Impedance plot obtained for $\text{PEO}_{10}\text{Eu}(\text{CF}_3\text{SO}_3)_3$, at 78 °C

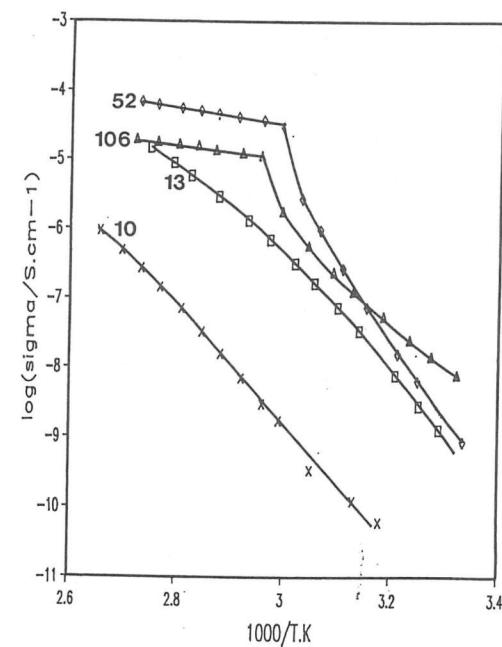


Figure 3. Conductivity behaviour as function of $1/T$ obtained for $\text{PEO}_x\text{Eu}(\text{CF}_3\text{SO}_3)_3$ polymer electrolyte with different salt concentrations ($x = 10, 13, 52$ and 106).

Conclusion

The reported results indicate that the PEO-Eu(CF₃SO₃)₃ electrolyte system described in this paper shows conductivity behaviour similar to that demonstrated by other divalent and trivalent cation based polymer electrolytes [17]. A more complete understanding of this complex system can only be achieved with further conductivity studies of intermediate compositions, dc polarisation studies (to determine the nature of the mobile species), the use of DSC and X-ray diffraction measurements and hot-stage polarising microscopy experiments, to assist in the construction of an accurate system phase diagram.

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