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Phase Diagram and Conductivity of the Polymer Electrolyte: $PEO_RLiCF_3SO_3$

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SUMMARY

A simple model for the concentration dependence of the electrical conductivity of the polymer electrolyte: poly(ethyleneoxide) - $LiCF_3SO_3$ is presented. It is assumed that the crystals with stoichiometry: 4 polymer oxygens to 1 lithiumion are insulating and the surrounding conducting solution is saturated in the 4:1 crystals. Correcting the space available for conduction with a volume correction factor accounts qualitatively for the concentration dependence of the conductivity.

Recent results (WESTON and STEELE 1981, OWEN 1982, PAPKE et al. 1981) on polymerelectrolytes of the type poly(ethyleneoxide) - (PEO) - alkali salts have shown that the conductivity depends strongly on the concentration, which is usually given as the ratio between the oxygens from the polymer and the cations added. When this ratio, R, approaches 4, the conductivity drops off rather sharply whereas at lower salt concentration, (higher R's), a diffuse maximum is observed in the conductivity.

WESTON and STEELE (1981, 1982) investigated both the $PEO_RLiCF_3SO_3$, (R=6, 8, 10) and the PEO_8LiClO_4 electrolytes and resolved a long standing discrepancy between the results of ARMAND (1978, 1979) and those obtained by most other workers. They showed that the use of high purity acetonitrile for the solvent casting, produces films (called 'high purity' films) without any signs of crystallinity whereas lower grade of acetonitrile give films ('low purity' films) containing crystalline regions embedded in an amorphous matrix.

The aim of the present paper is to present a simple model that accounts qualitatively for the concentration dependence of the conductivity of the 'low purity' type electrolytes.

These substances in general contain two phases (amorphous and crystalline) and two components (salt and polymer). Thus the composition in both phases must be fixed when the phases are in equilibrium. As to the composition of the crystalline phase it is now fairly well established (SHRIVER 1981) that four oxygens (from the polymer) coordinate one cation in a regular helical structure corresponding to R=4 in the crystals. In the amorphous phase the composition denoted R_{SAT} is unknown.

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Consider a mixture of S mol salt and P mol polymer (on a monomer basis). Let xS and yP be the amounts of salt and polymer forming the crystalline phase. The mass balances determining x and y are:

$$yP = 4\ xS$$

and

$$(1-y)P = R_{SAT}(1-x)S$$

giving:

$$x = \frac{R_{SAT} - R}{R_{SAT} - 4} \qquad \text{and} \qquad y = \frac{R_{SAT}/R - 1}{R_{SAT} - 4}$$

where R = P/S.

If the crystals are insulating their presence will reduce the effective space available for conduction. In the following very crude calculation we assume that both saturated solution and crystals have the same density: ρ. M_S and M_P are the molecular weights of the salt and the polymer repeat unit. Assuming the conductivity of the mixture of salt and polymer to be proportional to the volume fraction of the conducting saturated solution the apparent conductivity, σ_{AP} is given by:

$$\sigma_{AP} = \sigma_{SAT} \frac{(1-x)\ M_S\ S + (1-y)\ M_P\ P}{M_S\ S + M_P\ P}$$

$$= \sigma_{SAT} \frac{M_S + M_P\ R_{SAT}}{R_{SAT} - 4} \frac{R - 4}{M_S + M_P\ R}$$

This expression gives the conductivity as a function of R for saturated solutions containing crystals of 4:1 stoichiometry. For solutions below the saturation concentration the conductivity can be related to the sum of the diffusion coefficients of the individual ions, $D_1 + D_2$, through:

$$\sigma = \frac{(D_1 + D_2)\ F^2\ C}{RT}$$

where F, R and T have their usual meaning and C is the volume concentration of the salt.

If the diffusion coefficients are assumed to be concentration independent we obtain:

$$\sigma = \sigma_{SAT} \frac{C}{C_{SAT}}$$

where C_{SAT} is the saturation concentration.

As an example consider the results for the polymer electrolyte $PEO_R LiCF_3SO_3$ given by SØRENSEN and JACOBSEN (1982). If 1.39 is taken as C_{SAT} corresponding to R_{SAT}=16 and the measured conductivities for R=16 are used as σ_{SAT}, qualitative agreement is obtained between the experimental conductivities and the predicted ones: fig.1.

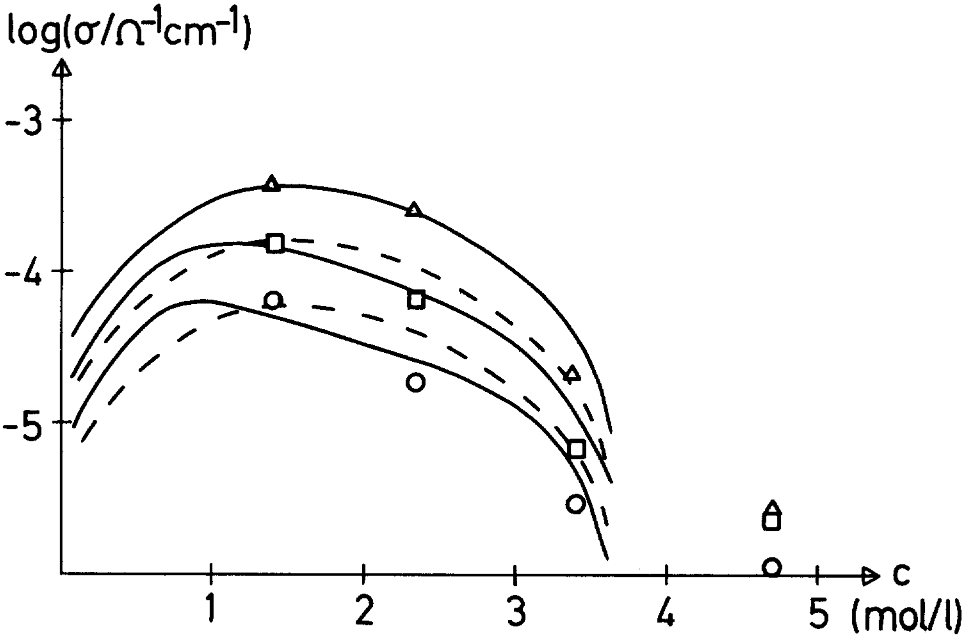

Figure 1. Experimental (open symbols) and calculated (solid and dashed lines) values of the conductivity of $PEO_RLiCF_3SO_3$ vs. volume concentration (ρ=1.2 g/cm^3).
△ : 125 °C, ☐ : 105 °C, ○ : 85 °C.
Dashed lines are calculated from constant R_{SAT} = 16.
Solid lines are calculated from:
R_{SAT} (125 °C) =16, R_{SAT} (105 °C) = 24,
R_{SAT} (85 °C) = 30

However, a temperature independent saturation concentration is inconsistent with the saturated solution hypothesis (see the schematic phase diagram, fig.2) and closer inspection of the conductivity data in fig.1 shows that only at 125 °C does the conductivity have its maximum at R=16.

At lower temperatures the maximum occurs at lower concentrations and rough estimates at 85 °C and 105 °C are: R_{SAT} (85 °C) = 24 and R_{SAT} (105 °C) = 30. When these values are used the solid lines in fig.1 are obtained. From this study we thus have values of R_{SAT} for three different temperatures. These are combined with the four points obtained by WESTON and STEELE (1981, table 1, third column) and shown in the solubility line of the phase diagram, fig.3.

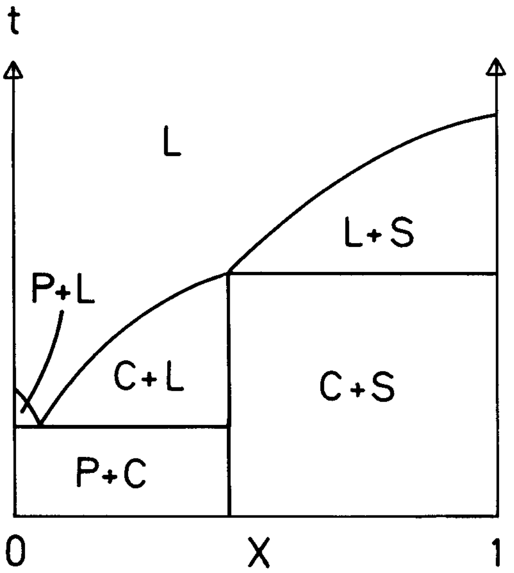

Figure 2. Schematic phase diagram for a polymer electrolyte contrary both crystalline (C) and amorphous (L) phases. The other phases are:
Pure salt (S)
Pure polymer (P)
X is the molfraction of Li to the total (Li + polymer oxygen) content

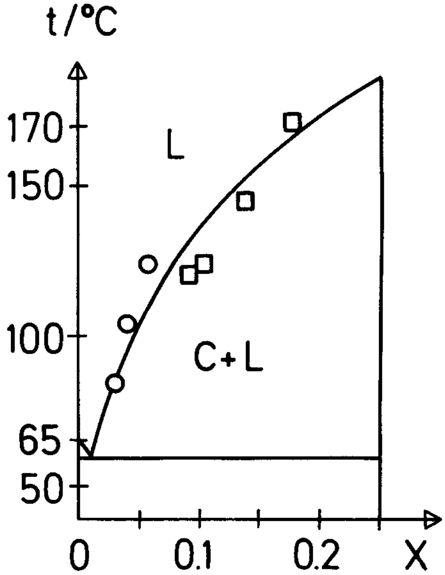

Figure 3. Solubility line of the phasediagram for the $LiCF_3SO_3$-PEO system.
□ are results obtained by WESTON and STEELE (1981).
○ are points obtained in the present study as explained in the text

The results of WESTON and STEELE (l.c.) further indicate the existence of an eutectic, melting at 60 °C (as opposed to the melting temperature of the pure PEO crystals: 65 °C) and a very rough extrapolation shows an eutectic composition of R=50.

On the above basis we conclude:

1. The polymer electrolyte $PEO_RLiCF_3SO_3$, ($4 \leq R \leq 50$), is adequately described by a phase diagram of the simple solvent (PEO)-solute ($LiCF_3SO_3$) type with one solvate (the stoichiometric complex), fig.2.
2. The stoichiometric 4:1 complex is a much poorer ionic conductor than the less concentrated saturated solution of the salt in the polymer.

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