

(a) Version date: 1997. 11. 28 (File name: b13ikedaman, Processed by WordPerfect Ver. 6.0aJ)

(b) Title: Multivalent cation conductive solid polymer electrolytes using photo-crosslinked polymers II.

Magnesium and zinc trifluoromethanesulfonates systems

(c) Authors: Shoichiro Ikeda, Yoichi Mori, Yuri Furuhashi, and Hideki Masuda

(d) Address: Nagoya Institute of Technology, Department of Applied Chemistry,
Gokiso-cho, Showa-ku, Nagoya 466, JAPAN

(e) Abstract: Solid polymer electrolytes have been composed of magnesium or zinc trifluoromethanesulfonates [$\text{Mg}(\text{CF}_3\text{SO}_3)_2$ or $\text{Zn}(\text{CF}_3\text{SO}_3)_2$], ethylene carbonate, and propylene carbonate impregnated in photo-crosslinked polymer of poly-(ethylene glycol) diacrylate which are reinforced by porous polypropylene membrane. Their conductivities are $1.7 \times 10^{-4} \text{ S cm}^{-1}$ at 1 mol% for $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, $2.1 \times 10^{-4} \text{ S cm}^{-1}$ at 4 mol% for $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, and $4.3 \times 10^{-4} \text{ S cm}^{-1}$ at 12 mol% for LiCF_3SO_3 systems at 25°C, respectively. The Arrhenius plots of them are almost linear between -5 and 55°C with 15-25 kJ/mol of activation energy for conduction.

(f) Key words: Photo-crosslinked polymer, Zinc trifluoromethanesul-

fonate, Magnesium trifluoromethanesulfonate, Solid polymer electrolytes, Tetraethylene glycol diacrylate.

(g) Chemical compounds: LiCF_3SO_3 , $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, tetraethylene glycol diacrylate, poly-(ethylene glycol) diacrylate.

(h) Corresponding author: Shoichiro Ikeda, Nagoya Institute of Technology, Department of Applied Chemistry, Gokiso-cho, Showa-ku, Nagoya 466-8555, JAPAN.

Fax. +81-52-735-5247, e-mail: ikeda@ach.nitech.ac.jp

1. Introduction

It has been well known that poly-(ethylene oxide) [abbreviated as PEO] forms ionic-conductive complexes, i.e. solid polymer electrolytes [SPEs] [1], with salts of mono-, di-, or trivalent metals. However, those values are relatively low in the range of 10^{-5} to 10^{-8} S cm^{-1} at ambient temperature [2, 3]. Recently, K.M. Abraham et al. [3] reported the electrical conductivities of photo-crosslinked poly-(ethylene glycol) diacrylate [PEGDA] based solid polymer electrolytes with lithium salts reinforced by the micro-porous membranes, i.e. Celgard[®].

We have reported the results on the application of this procedure to the multivalent cation salts, such as zinc halides [4], where the electrolyte of ZnI_2 (8 mol%) + ethylene carbonate [EC] (28 %) + propylene carbonate [PC] (28 %) + tetraethylene glycol dimethyl ether [tetraglyme] (28 %) + tetra-

ethylene glycol diacrylate [TEGDA] (8 %) reinforced by Celgard[®] #2500 has the electrical conductivity of $4.3 \times 10^{-5} \text{ S cm}^{-1}$ at 25 °C.

In this paper, we will present the results on the magnesium and zinc trifluoromethanesulfonates [triflate] $[\text{Mg}(\text{CF}_3\text{SO}_3)_2]$ and $[\text{Zn}(\text{CF}_3\text{SO}_3)_2]$ systems with EC, PC, and TEGDA except for tetraglyme, comparing with the previous results on the zinc halide systems [4]. Their conduction behavior has also been compared with that of the lithium triflate system.

2. Experimental

The Celgard[®] membrane-reinforced solid electrolytes were prepared in the same manner as the paper reported by K.M. Abraham et al. [3] and our previous paper [4]. Namely, precursor solutions were composed of $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ [Fluka, >98%] or $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ [Fluka, >98%], EC [TCI, EP Grade], PC [Kishida Chem., GR Grade], and TEGDA [Aldrich]. A photoinitiator, Darocur[®] 1170, was donated by Japan Ciba Gygi. A few drops of Darocur[®] were added to the precursor solutions of $[\text{EC} : \text{PC} : \text{TEGDA} = 73 : 16 : 3]_{100-x} [\text{M}(\text{CF}_3\text{SO}_3)_n]_x$. The Celgard[®] #3401 membranes, 10 mm × 10 mm, 25 μm thick, and porosity of 38% donated by the former dealer in Japan; Polyplastics Co., were soaked over night in the precursor solutions put in Teflon[®] FEP culture dishes which were stored in a dark box placed in a dry box [UNICO, UN-650F] filled with dried N₂ gas. They were then clamped between two Pyrex[®] glass plates and irradiated with an UV light (λ = 366 nm) [UVP Inc., UVL-21] for about 10 min to polymerize TEGDA to PEGDA. The

electrolyte with LiCF_3SO_3 [Kishida Chem., GR Grade] was also prepared for comparison.

The conductivity of the Celgard[®]-reinforced electrolyte bounded two stainless steel disk electrodes was determined with an AC bridge [DELICA Elec. Meas. Instr., Mini Bridge D1S] with 0.5 V of 20 kHz between -5 and 55 °C using a gastight cell made of Neoflon[®] CTFE, stainless steel, and O-rings. The specimen was set into the cell in the dry-box. The measuring frequency has been determined from the preliminary experimental results using a frequency response analyzer [Solartron, 1255] between 1 Hz and 2 MHz.

The differential scanning calorimetry [DSC] analysis of the electrolytes was conducted for the zinc system between -100 and +100°C at ± 10 K / min using a Rigaku, DSC8230L type analyzer in order to characterize the thermal property of the electrolytes at the bulk and the Celgard[®] reinforced states.

The potential window of the electrolyte with 4 mol% Zn triflate reinforced by the Celgard[®] membrane was measured by using a Zn | [EC: PC : TEGDA = 73 : 16 : 3]₉₆ [Zn(CF₃SO₃)₂]₄ + Celgard[®] #3401 | Glassy carbon cell with a potentiostat [Hokuto Denko, HA-301] and a function generator [Hokuto Denko, HB-111] at a scan speed of 10 mV/s. The output signals were acquired at 0.2 s/cycle and treated by a conventional micro-computer system.

3. Results and Discussion

Each metal triflate was dissolved up to 8, 6, or 16 mol% in the precursor solutions for the system of Mg, Zn, or Li, respectively. The prepared polymer electrolyte was a quasi-solid phase as a bulk and a Celgard[®]-reinforced state, of which thickness was 25 to 36 μm .

Figure 1 shows a typical example of the preliminary experimental results on complex impedance measurements using the frequency response analyzer between 1 Hz and 2 MHz (but drawn up to 20 kHz for clarity) for 4 mol% $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ system using stainless steel electrodes. At 20 kHz, the semicircle intercepts the axis, of which value corresponds to the bulk resistance of the electrolyte. From this figure, 20 kHz has been selected as the measuring frequency of the AC bridge.

The Arrhenius plots of the conductivities of the electrolytes are shown in Figs. 2, 3, and 4 for Li, Mg, and Zn systems, respectively, where the conductivity values were not corrected with the membrane tortuosity defined by K.M. Abraham et al. [3]. They are almost linear between -5 and 55°C with 15-25 kJ/mol of the activation energy for conduction, suggesting the conduction mechanism of the electrolytes, i.e. carriers of which migrate in the solvent molecules of a quasi-solid gel phase impregnated in the polymer matrix of PEGDA [5] but do not by the help of the segmental movement of polymer according to the Williams-Landel-Ferry [WLF] equation [6] such as the PPO- LiClO_4 system [7].

The conductivity values at 25°C are plotted against to the concentrations of metal salts in Fig. 5. Between 1 and 6 (Mg) or 1 and 8 (Zn) mol% of metal salts, their ionic conductivities are in the same order of that for

LiCF₃SO₃ system, i.e. 10⁻⁴ S cm⁻¹ at 25°C. The maxima of the conductivities were obtained 1.7 × 10⁻⁴ S cm⁻¹ at 1 mol% for Mg(CF₃SO₃)₂, 2.1 × 10⁻⁴ S cm⁻¹ at 4 mol% for Zn(CF₃SO₃)₂, and 4.3 × 10⁻⁴ S cm⁻¹ at 12 mol% for LiCF₃SO₃ system, respectively. Their tendencies are also similar and clearer at 55°C. These values are almost one order greater than those of the halides system reported previously [4]. The reason of this fact is thought to be due to the higher dissociation constant of triflate anion than the halide anion. At the low metal salt contents of 1 mol%, the electrical conductivities were the order of Mg > Zn > Li salts, i.e. conductivities of divalent salts were greater than that of monovalent salt. Between 2 and 4 mol%, the conductivities were almost the same values for all salts. The concentration of the metal salt showing the maximum conductivity differs depend on the kind of the metal.

It is suggested that the carrier in the electrolyte is the ions produced by dissociation of dissolved salts in the solvent molecules of a quasi-solid gel phase impregnated in the polymer matrix, because more than one order increase in the conductivity is observed by addition of metal salts of 1 mol%. The carrier of the metal salt free sample is not clear but is thought to be partially due to the remaining proton and hydroxyl ions.

For divalent salts, the activation energy become higher over the concentration showing the maximum conductivity as shown in Fig. 6. The reason of the lower conductivity and higher activation energy at the higher salt concentration for divalent metals is thought to be due to the higher

interaction among the metal ions, which restricts the movement of themselves.

The DSC curves showed the so-called melting points of EC and PC at 258 to 273 K depend on the content of the metal salt as shown in Fig. 7 for the bulk Zn triflate systems. In downward measurements, supercooling was observed at 6 and 8 mol% Zn triflate. By reinforcing in Celgard® #3401 membranes, the melting points were slightly raised than those of the bulk systems as shown in Fig. 8. There is a tendency that the electrolyte having the higher melting point shows the higher conductivity, except for 8 mol%, which showed a relatively large supercooling.

Figure 9 shows the cyclic voltammogram of the polymer electrolyte with 4 mol% Zn triflate reinforced with the Celgard® membrane measured by using the Zn | [EC: PC : TEGDA = 73 : 16 : 3]₉₆ [Zn(CF₃SO₃)₂]₄ | Glassy carbon cell. The potential window was between -0.20 V and +1.80 V vs. Zn/Zn²⁺. Namely, Zn triflate-EC-PC-PEGDA-Celgard® system has a potential window of 2.0 V. The width of windows increased with time, because of the growth of passivation films. After a several cycles, however, the width of window slightly decreased in both sides. The zinc plating/dissolving process appears irreversible with a noticeable overvoltage. The nucleation loop characteristic of metallic deposition by growth of nucleation sites is observed. While the cell Zn | SPE + Celgard® | Zn showed a lower overvoltage and a reversibility with a smaller window width.

Conclusion

By changing the anion of the divalent metal salts containing solid polymer electrolytes impregnated in photo-crosslinked polymer from halides to triflate, the electrical conductivity became higher as $2.1 \times 10^{-4} \text{ S cm}^{-1}$ in the case of 4 mol% $\text{Zn}(\text{CF}_3\text{SO}_3)_2$. The polymer system of magnesium triflate also shows a high conductivity as $1.7 \times 10^{-4} \text{ S cm}^{-1}$ at 1 mol%. The potential window of the electrolyte for Zn triflate system is 2.0 V from the cyclic voltammogram of a Zn | [EC: PC : TEGDA = 73 : 16 : 3]₉₆ [$\text{Zn}(\text{CF}_3\text{SO}_3)_2$]₄ | Glassy carbon cell.

Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research (C) (No. 06650944) from The Ministry of Education, Science, Sports and Culture of Japan.

References

- [1] P.V. Wright, Br. Polymer J., 7 (1975) 319.
- [2] D. Baril, Y. Chabre, and M.B. Armand, J. Electrochem. Soc., 140 (1993) 687.
- [3] K.M. Abraham, M. Alamgir, and D.K. Hoffman, J. Electrochem. Soc., 142 (1995) 683.
- [4] S. Ikeda, Y. Mori, Y. Furuhashi, and H. Masuda, Denki Kagaku, 65 (1997) 780.
- [5] E. Tsuchida, H. Ohno, and K. Tsunemi, Electrochim. Acta, 28 (1983) 591.

[6] M.L. Williams, R.F. Randel, and J.D. Ferry, *J. Am. Soc.*, 77 (1955) 3701.

[7] M. Watanabe, A. Suzuki, K. Sanui, and N. Ogata, *Nippon Kagaku Kaishi*, 1986 (1986) 428.

Figure captions

Fig. 1. Cole-Cole plot of the preliminary experimental results on the solid polymer electrolyte [EC: PC : TEGDA = 73 : 16 : 3]₉₆ [Zn(CF₃SO₃)₂]₄ using a frequency response analyzer.

Fig. 2. Arrhenius plots of the electrical conductivity of solid polymer electrolytes with LiCF₃SO₃ system reinforced by Celgard® #3401 membranes.

Fig. 3. Arrhenius plots of the electrical conductivity of solid polymer electrolytes with Mg(CF₃SO₃)₂ system reinforced by Celgard® #3401 membranes.

Fig. 4. Arrhenius plots of the electrical conductivity of solid polymer electrolytes with Zn(CF₃SO₃)₂ system reinforced by Celgard® #3401 membranes.

Fig. 5. Electrical conductivity of solid polymer electrolytes with LiCF₃SO₃, Mg(CF₃SO₃)₂, and Zn(CF₃SO₃)₂ systems reinforced by Celgard® #3401 membranes with respect to the metal salt concentration measured at 25 °C.

Fig. 6. The activation energy for electrical conduction of solid polymer electrolytes with LiCF₃SO₃, Mg(CF₃SO₃)₂, and Zn(CF₃SO₃)₂ systems rein-

forced by Celgard® #3401 membranes with respect to the metal salt concentration.

Fig. 7. DSC curves for the bulk solid polymer electrolytes with Zn $(\text{CF}_3\text{SO}_3)_2$ system. Started from 173 K at 10 K / min.

Fig. 8. So-called melting points of solid polymer electrolytes with Zn $(\text{CF}_3\text{SO}_3)_2$ system bulk and reinforced by Celgard® #3401 membranes with respect to the metal salt concentration.

Fig. 9. Cyclic voltammogram of the zinc plating/stripping process from the $[\text{EC} : \text{PC} : \text{TEGDA} = 73 : 16 : 3]_{96} [\text{Zn}(\text{CF}_3\text{SO}_3)_2]_4$ electrolyte reinforced by Celgard® #3401 membrane between a Zn plate and a glassy carbon electrodes at 25 °C; scan rate of 10 mV/s, reference electrode: Zn/Zn²⁺.

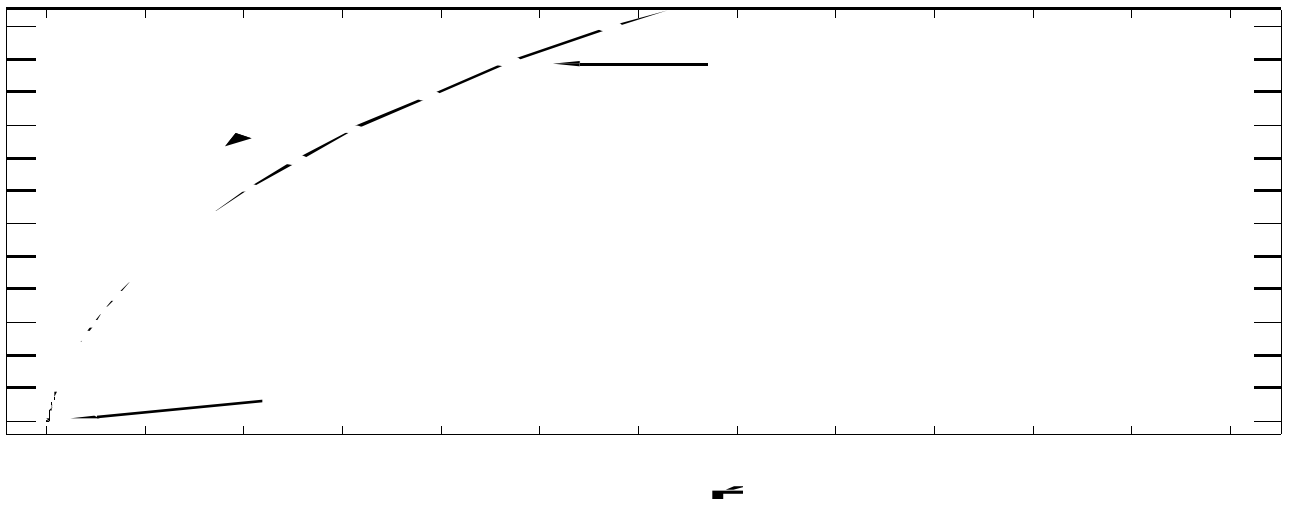


Fig. 1

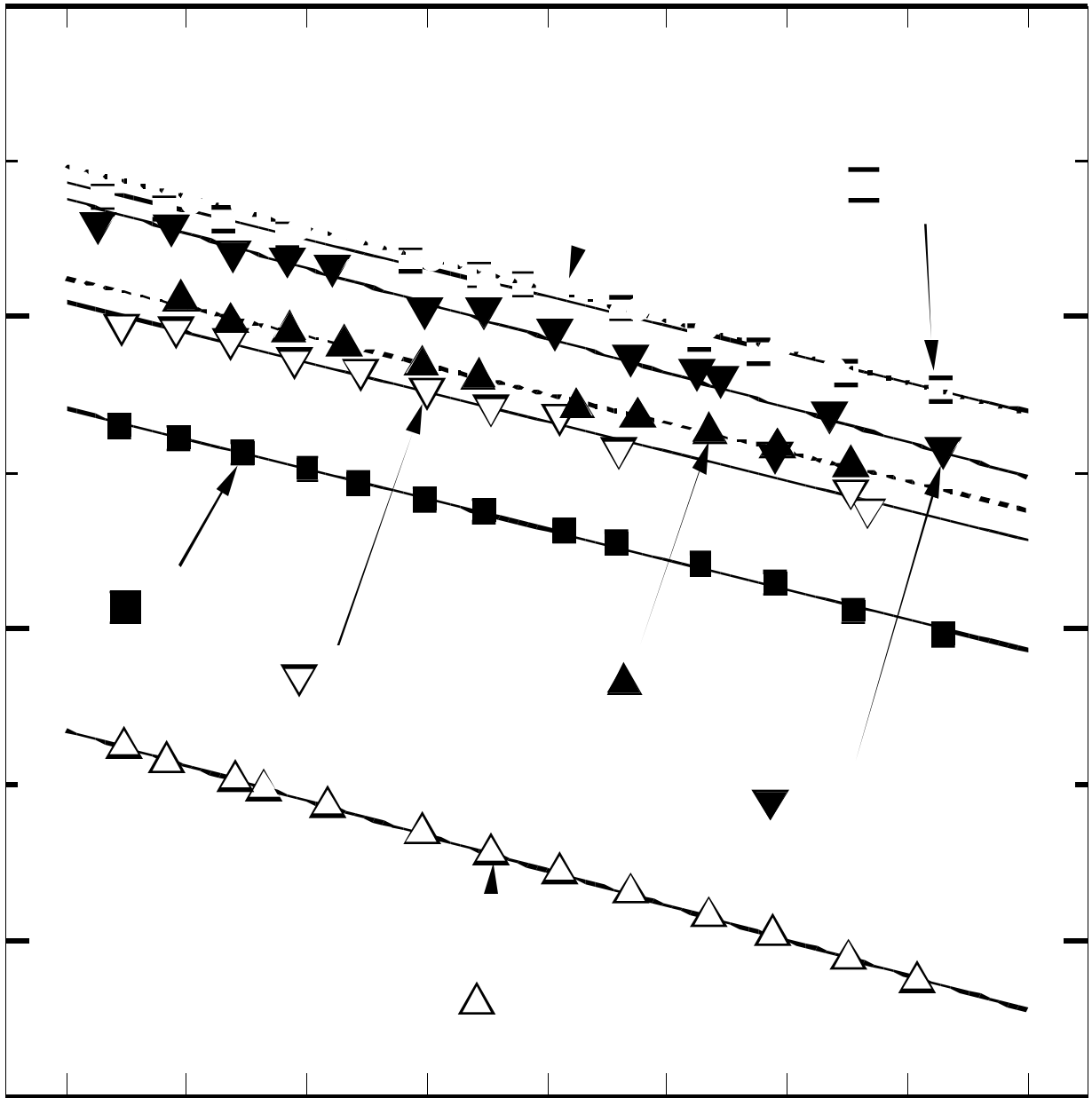


Fig. 2

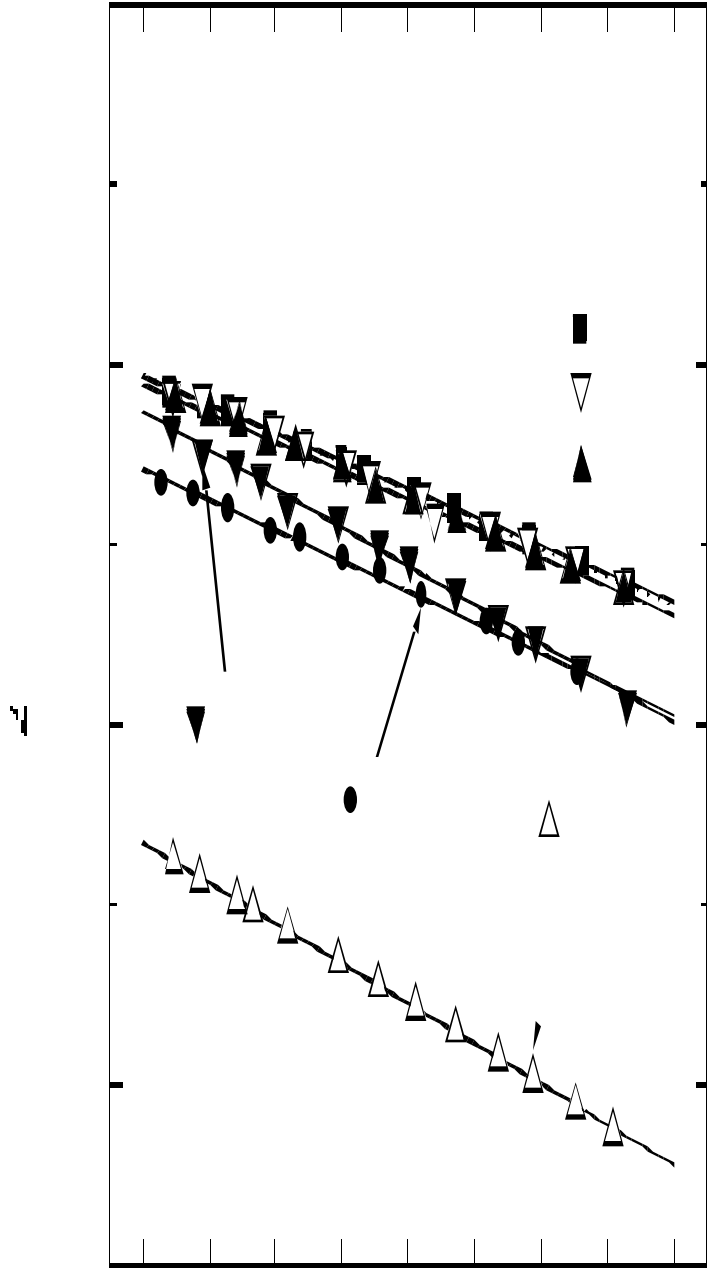


Fig. 3

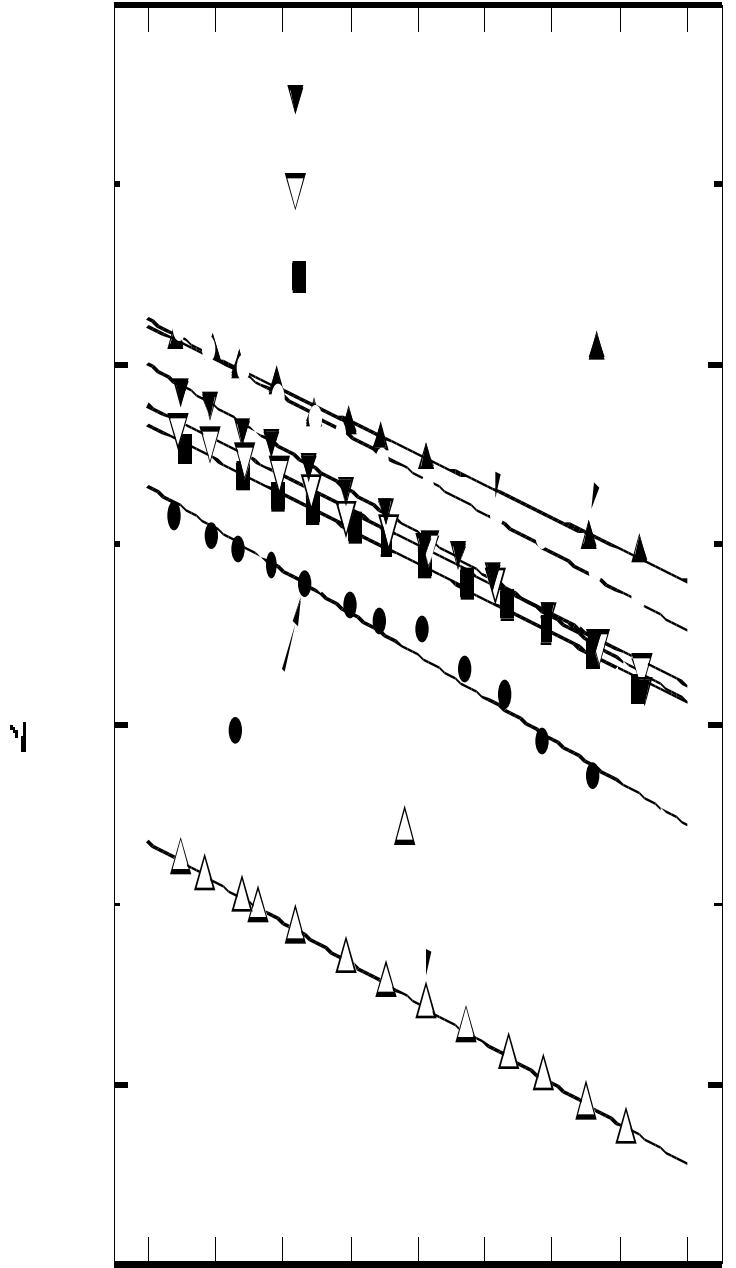


Fig. 4

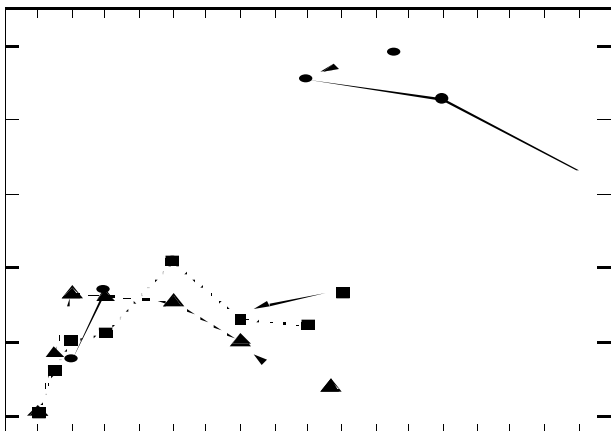


Fig. 5

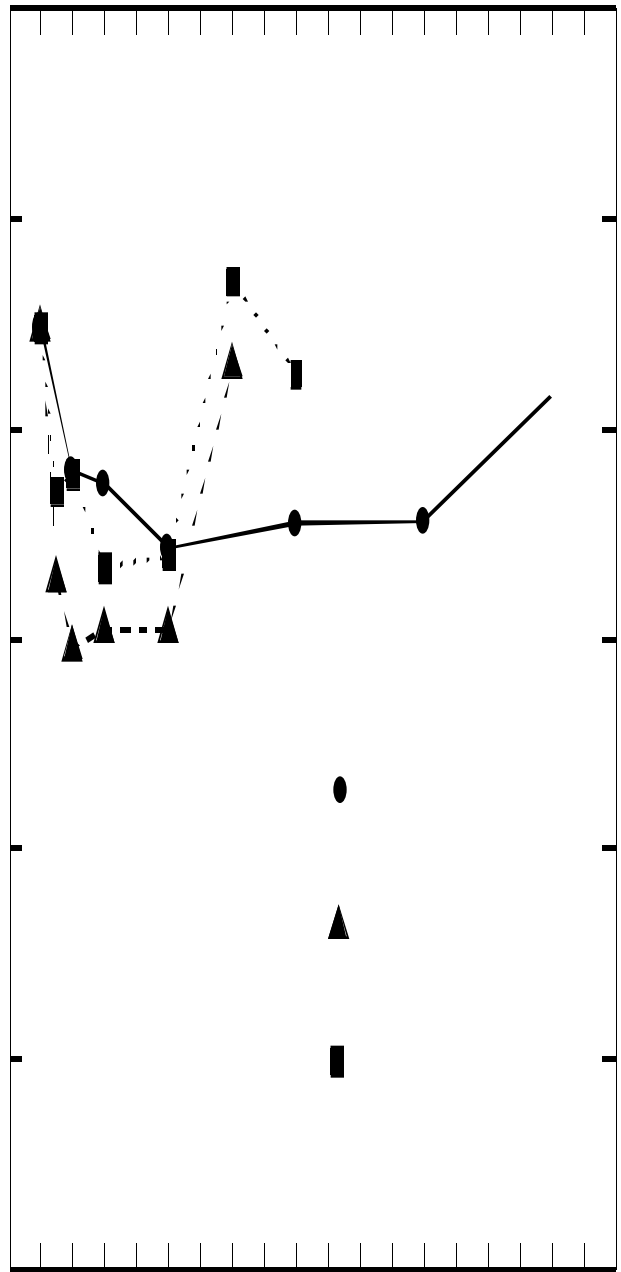


Fig. 6

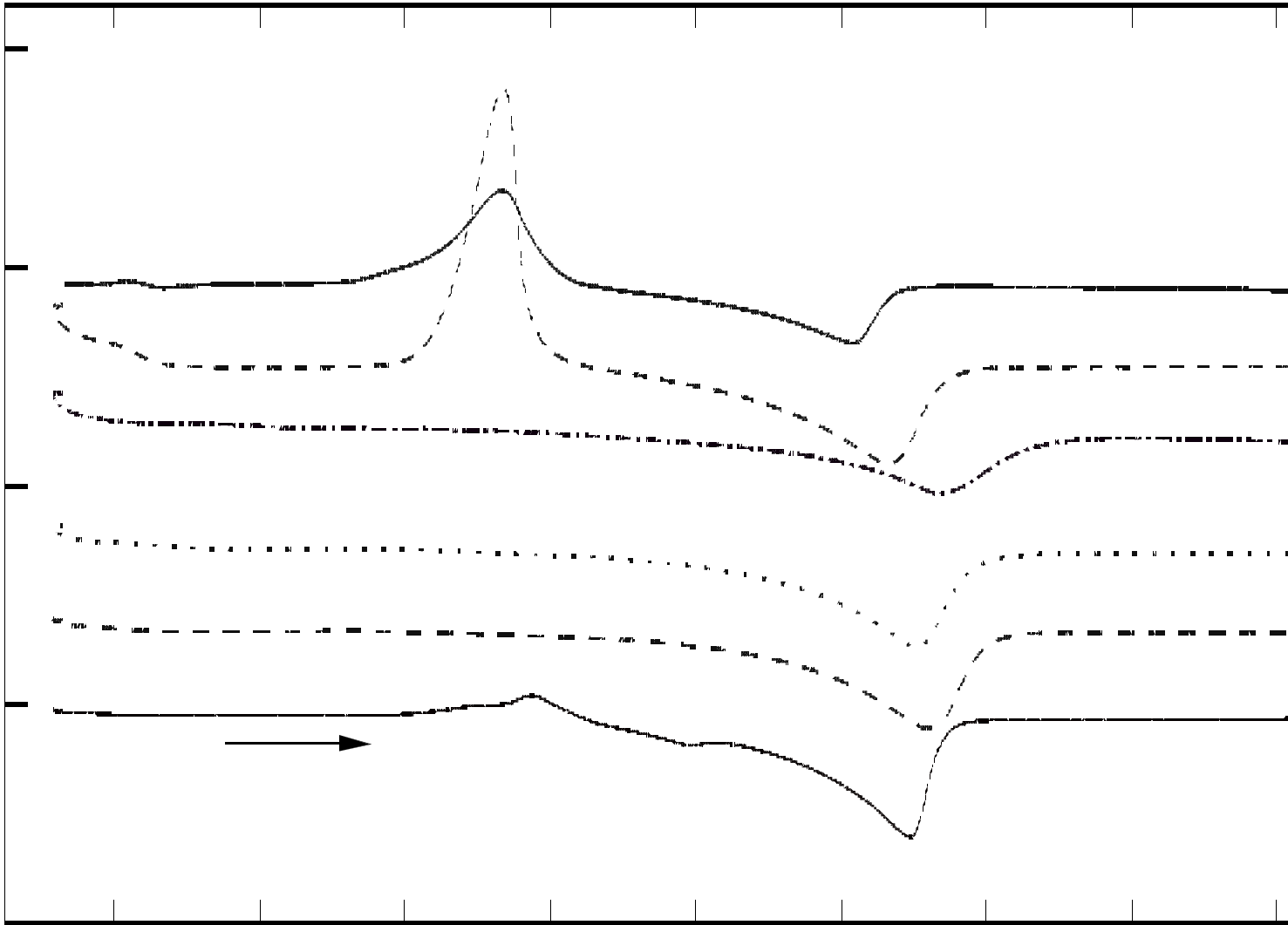


Fig. 7

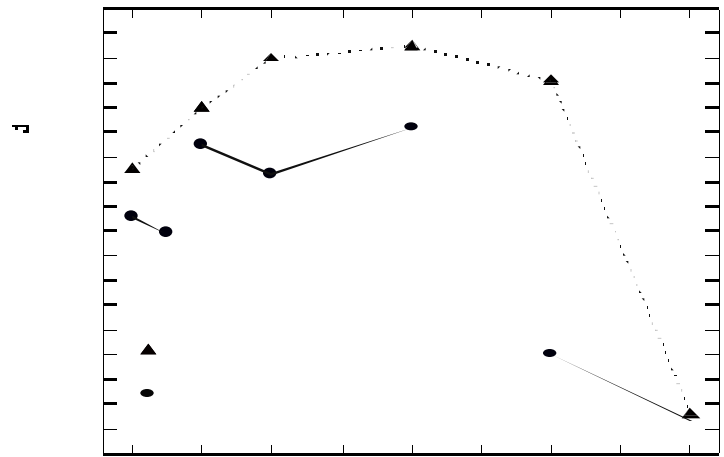


Fig. 8

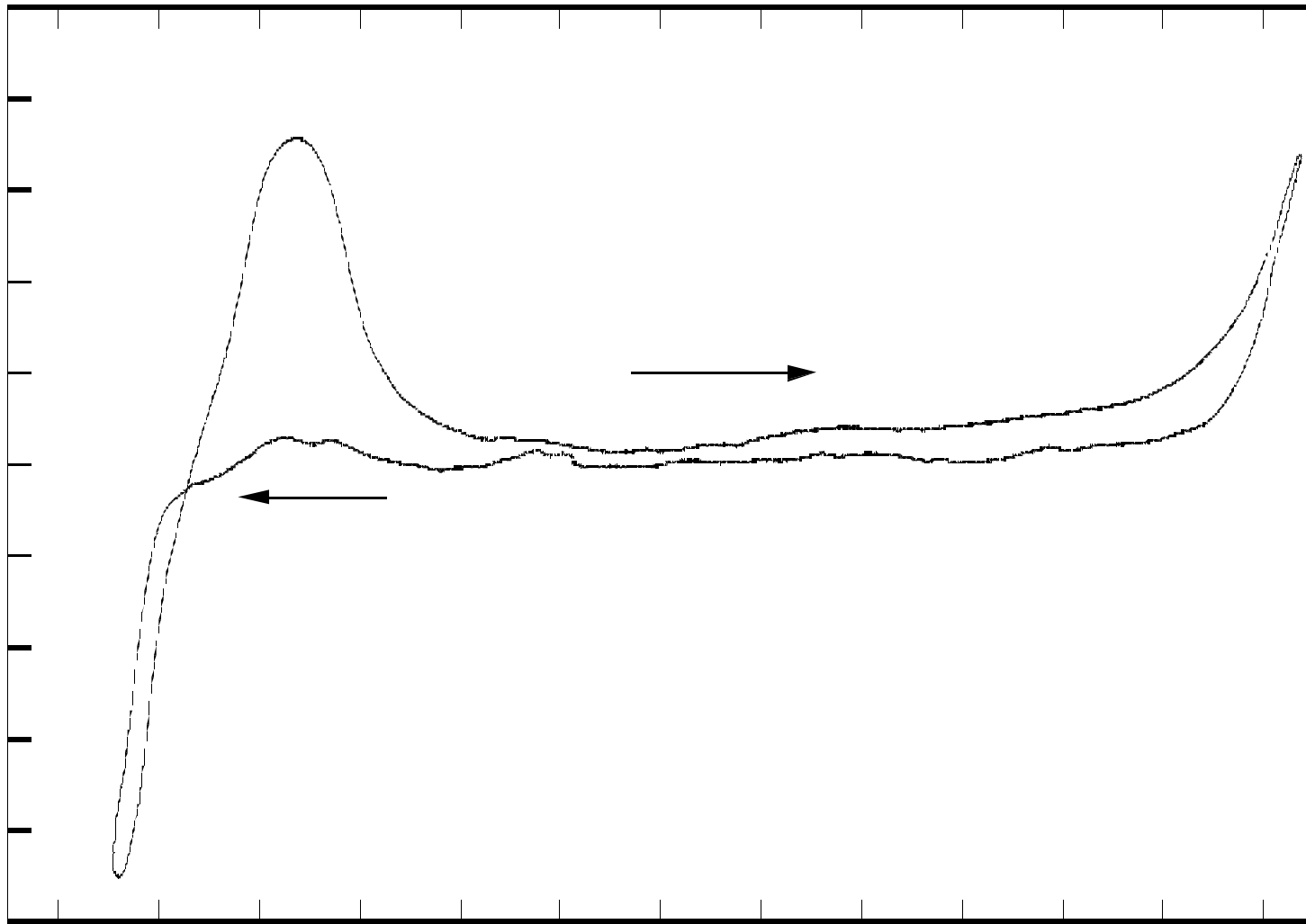


Fig. 9