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IONIC CONDUCTIVITY OF ORGANOSULFUR MELTS FOR ADVANCED STORAGE ELECTRODES

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ABSTRACT

Organosulfur melts show promise as positive electrodes for advanced storage batteries. The attainable energy efficiency and power density of a secondary battery is directly related to polarization losses in the cell under load. One of the contributing factors to polarization of an organosulfur electrode is the rate of ionic transport in the melt. Among the sodium/organosulfur batteries under investigation in this laboratory is the sodium/beta"-alumina/(tetraethylthiuram disulfide) cell, in which the product of cell discharge is the thiolate salt, sodium diethyldithiocarbamate (NaDEDC). Accordingly, the ionic conductivity of NaDEDC and related electrolytes in molten tetraethylthiuram disulfide (TETD) has been studied as a function of composition and temperature. The ionic conductivity of a NaDEDC/TETD melt of composition corresponding to 2 % discharge of a Na/TETD battery was determined to be 2×10^{-5} (ohm cm)$^{-1}$ at 130°C which increases to 1×10^{-3} (ohm cm)$^{-1}$ for a melt corresponding to 28 % discharge. The discharge data for Na/TETD batteries indicates that ionic conductivity of the positive electrode melt contributes negilible polarization after a few percent of cell discharge, indicating that ionic conductivity in the above range is acceptable for energy-efficient operation of these cells over nearly the entire compositional domain. The relationship between the equivalent conductivity of these melts and concentration is also discussed as well as the implications of the measured viscosity of the pure TETD melt.

INTRODUCTION

The recent introduction of a large class of organosulfur compounds offering unique properties as positive electrodes in advanced batteries (1) has prompted investigations into the physicochemical and electrochemical properties of these materials. The organosulfur electrodes are based on the chemically reversible oxidation of alkali metal thio salts to the corresponding disulfides, $2\ RS^- \rightleftharpoons RSSR + 2\ e^-$, where R is an organic moiety. Previous work on sulfur based cathodes has been limited to *inorganic sulfur salts*, either operating at high temperatures such as the Na/S cell (2,3), or dissolved in organic solvents to reduce the cathode operating temperature (4), or dissolved in chloroaluminate melts (5). The attraction of a generic organic redox couple for battery applications includes the ability to manipulate the physical properties such as liquidus range, viscosity, dielectric constant, etc., as well as the electrochemical properties, through careful choice of the organic moiety. For example, the melting points of representative disulfides tested in intermediate temperature sodium cells range from -85°C for dimethyl disulfide (DMDS) to 74°C for tetramethyl thiuram disulfide (TETD), with viscosities ranging from less than 10 centipoise for the alkyl disulfides to high viscosity polymers such as $-(SCH_2CH_2SSCH_2CH_2S)-_n$, and solvating power for sodium ion salts ranging from close to 50 mole% for TETD and hydroxyethyldisulfide to negligible for dimethyldisulfide (1,6).

To optimize the energy efficiency and power density of the Na/RSSR cells, it is imperative to minimize the polarization losses during charge/discharge cycling. One of the contributing factors to cell polarization is the ohmic

drop associated with ionic transport in the cell under load. Since the RSSR melts are essentially non-conductive prior to generation of the thio salts during cell discharge it is instructive to determine the increase in ionic conductivity of these melts as a function of composition. The present paper concerns the ionic conductivity of tetraethylthiuram disulfide (TETD) as a function of concentration of sodium diethyldithiocarbamate (NaDEDC). The cell reaction for a Na/TETD cell is,

$$(C_2H_5)_2N\overset{\overset{\displaystyle S}{\|}}{C}-S-S-\overset{\overset{\displaystyle S}{\|}}{C}N(C_2H_5)_2 + 2\ Na \rightleftharpoons 2\ Na\overset{\overset{\displaystyle S}{\|}}{C}N(C_2H_5)_2.$$

TETD NaDEDC

Batteries of this type have been assembled in the 100 % charged state (pure TETD positive electrode) (1,7) with a cell design similar to the Na/S battery where the liquid sodium negative electrode is separated from the positive organosulfur electrode by a sodium-ion conductive ceramic separator, beta"-alumina. When such a cell is placed under load, the instantaneous cell voltage drop observed is due to charge-transfer resistance in the positive electrode and ohmic losses in the cell. The largest ohmic losses in the cell are undoubtably due to ionic transport across the ceramic electrolyte and ionic transport in the positive electrode. At 130°C with 20 cm^2 electrolyte surface area a beta"-alumina electrolyte tube of 1 mm thickness contributes approximately 0.2 ohms to the cell resistance (6). The internal resistance of a fully charged Na/TETD cell, as measured by millisecond current pulses, is initially from 40 to 100 ohms and rapidly decreases on cell discharge to between 0.6 and 2 ohms, depending on current load and art of assembly (1,6). The rapid drop in cell resistance upon discharge is almost certainly due to the generation of NaDEDC salt in the positive electrode, thereby increasing the ionic conductivity of the melt. In all cases, the resistivity-drop levels off within a few percent of cell discharge indicating that ionic conductivity increases beyond that achieved at 2 % discharge does not significantly reduce

ohmic losses in the cell. This was further supported by addition of solvents to the positive electrode known to increase its ionic conductivity but which did not affect the ohmic drop in the cell (7). Therefore, given the present cell configuration, it appears that the magnitude of the voltage drop of the Na/TETD cell under load is initially determined by the ionic resistivity of the positive electrode melt; however, beyond about 2 % discharge the key parameters are the resistance of the beta"-alumina tube (≈ 0.2 ohms) and the electron-transfer overpotential of the positive electrode (non-ohmic). The results below characterize the ionic conductivity of these NaDEDC/TETD melts.

EXPERIMENTAL

Reagent grade anhydrous solvents including dimethyl sulfoxide (DMSO), bis methoxyethyl ether (diglyme), and tetramethyl urea (TMU), were stored over molecular sieves prior to use. Reagent grade tetraethylthiuram disulfide (TETD) was recrystallized four times from butanol to yield pale yellow needles which were dried under vacuum. Reagent grade sodium diethyldithiocarbamate (NaDEDC) and sodium dimethyldithiocarbamate (NaDMDC) were dried under vacuum at 70°C for two days prior to use. Reagent grade tetracyanoethylene (TCNE), tetracyanoquinodimethane(TCNQ), and sodium trifluoromethane sulfonate (NaTFMS) were used as recieved. Tetrabutylammonium diethyldithiocarbamate (TBADEDC) was prepared by precipitation of the TBADEDC salt upon mixing aqueous solutions of tetrabutylammonium perchlorate (TBAP) and sodium diethyldithiocarbamate; the precipitated salt was dried under vacuum for 3 days. All above reagents were purchased from Aldrich Chemical Company, with the exception of NaTFMS and TBAP which were obtained from Alfa Products.

The complex impedance of organosulfur melts was analyzed with a Hewlett-Packard 3312A Signal Generator and a Hewlett-Packard 3575A Gain- Phase Meter

in the frequency range of 1 to 10^6 Hz. The conductivity cell consisted of matched, shielded, parallel platinum electrodes with a cell constant of 1.85 ohm•cm, immersed in the organosulfur melt. The ionic conductivities of the organosulfur melts were determined from the real axis intercept of the complex impedance. The conductivity of the NaDEDC and related electrolytes was determined in a variety of solvents including molten TETD, DMSO, and Diglyme.

The viscosity of molten TETD was determined as a function of temperature with an Ostwald viscometer placed inside a temperature regulated transparent quartz funace.

RESULTS AND DISCUSSION

The conductivity of pure molten TETD is approximately 2×10^{-7} at 130°C (table 2). This is clearly too low to permit significant current flow in a TETD melt, as evidenced by the large internal resistance of a fully charged Na/TETD cell (1,6,7). The ionic conductivity of NaDEDC in molten TETD at 130°C is presented in Table 1 and figures 1 and 2. Figure 1 shows a smooth increase of the melt conductivity with increasing concentration of electrolyte, reaching a value of 1×10^{-3} for a 3.7M solution, which would correspond to 28% discharge of the TETD electrode in a sodium anode battery, and representing four orders of magnitude change from the conductivity of the neat melt. The ionic conductivity of the NaDEDC/TETD melt corresponding to 2 % discharge was 2×10^{-5} $(\text{ohm cm})^{-1}$ (table 2). During discharge of a Na/TETD cell, the concentration of NaDEDC at the beta"-alumina/graphite felt interface would undoubtably be greater than in the bulk of the electrode due to slow diffusion of the salt; still, the conductivity behavior shown in figure 1 is sufficient to decrease rapidly the contribution of ionic resistivity to total cell resistance.

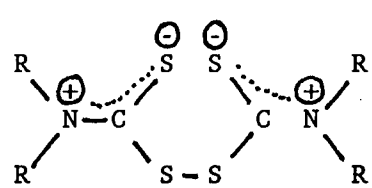
The equivalent conductivity, $\Lambda=\sigma/c$ (c is in equivalents/cm^3 and σ is in (ohm

cm^{-1})), or the conductivity per ion for NaDEDC, is plotted against the square root of concentration in figure 2. For most aqueous solutions of strong electrolytes (HCl, KNO_3, NaDEDC, etc.), there is a characteristic linear decrease of equivalent conductivity with increasing $(\text{concentration})^{1/2}$ due to the increasing importance of ion-ion interactions as expressed the empirical law of Kohlrausch*,

$$\Lambda = \Lambda_o - k_c c^{1/2}$$

where Λ_o is the extrapolated equivalent conductance at infinite dilution, and k_c is an experimental constant. Deviations from Kohlrausch behavior occur for weak electrolytes and/or at high electrolyte concentrations, where ion association becomes increasingly important. The behavior observed in figure 2 implies a conductivity minimum at about .06M, and a subsequent increase in equivalent conductivity with increasing concentration. It is well known that significant ion pairing occurs for electrolytes dissolved in non-aqueous solvents of low-dielectric constant, and that at sufficiently low values of ϵ and high electrolyte concentration the formation of triplet ions is favored, resulting in a Kohlrausch plot with a conductivity minimum as seen in figure 2.

Although TETD is able to solvate NaDEDC quite well, dissociation of the salt into separate ionic species is largely determined by the magnitude of the dielectric constant of TETD, which presumably is fairly low. The ability of thiuram disulfides to solvate electrolytes is most likely due to partial charge separation as shown below,



this relationship can also be derived theoretically as the Debye-Huckle-Onsager Equation (8).

which follows from NMR investigations (9). This solvation process is analogous to charge separation postulated for the amides (10), although they contain the far more polar -C=O group (as opposed to -C=S) and consequently exhibit high dielectric constants and great dissociating power for electrolytes.

Evidence of substantial ion-pairing in TETD is further supported by the magnitude of the equivalent conductivity. The range of Λ seen in figure 2 is between .08 and .3 ($ohm^{-1}cm^{2}equiv^{-1}$), whereas values for strong electrolytes in aqueous solutions are of the order of 100. The addition of a small volume of 1,1,3,3 tetramethylurea (ϵ=23) increased the equivalent conductivity of NaDEDC in TETD (fig 2) , due to either a decrease in ion pairing or increase in ion mobility in the melt.

The equivalent conductivity of NaDEDC dissolved in DMSO (ϵ=47) at room temperature is shown in figure 3. Although the data are limited to a few points, two observations can be made: first, the equivalent conductivity appears to follow Kohlrausch's law; second, the values of Λ are approximately two orders of magnitude higher than for NaDEDC in TETD at 130°C. Measurements were also made for NaDEDC dissolved in a low dielectric constant solvent, bis(2-methoxyethyl) ether ($\epsilon\approx7$), at room temperature. As is evident from the few data in figure 4, Λ increases with increasing concentration, again indicating formation of triplet ions. Further, the magnitude of the equivalent conductivity in the ether is of the order of NaDEDC in TETD. The similarity of the equivalent conductivities in the two solvents indicates that NaDEDC may be dissociated to the same extent by the two solvents, which would imply a dieletric constant close to that of the ether. However, it is likely that mobility of the ions plays a big role in the measured conductivities in TETD, since the melts were noticeably viscous.

The measured viscosity of molten TETD as a function of temperature is shown in figure 5. The viscosity of TETD is strongly temperature dependant and ranges

from 54 centipoise at 75°C (m.p.= 74°C) to 10 centipoise at 130°C. Dimethyl sulfoxide and diglyme both have viscosities of approximately 1 centipoise at room temperature. The high viscosity of TETD at 130°C implies lower mobilites for both ionic and neutral species in the TETD melts. The equivalent conductivities of NaDEDC in both TETD and diglyme are in the same range, which is probably due to greater dissociating power of TETD as a solvent for NaDEDC, which is offset by higher melt viscosity.

The effect of temperature on the conductivity of NaDEDC solutions is shown in figures 6 and 7. The dependence of the conductivity of the NaDEDC/TETD melt on temperature is not as dramatic as the temperature dependance of TETD melt viscosity, but it is greater than the temperature dependence of the conductivity of the NaDEDC/diglyme solution. Although the variation of diglyme viscosity with temperature was not determined, it is quite doubtful that it would be as large as was observed with TETD. Accordingly, the greater temperature dependence of the ionic conductivity of NaDEDC in TETD is most likely due to a greater rate of change of ionic mobility with temperature.

The ionic conductivities of other electrolytes in TETD are displayed in Table 2. A couple of observations are worth noting. One point is that while liquid TETD is quite capable of dissolving and dissociating a variety of dithiocarbamate salts such as NaDEDC, NaDMDC, and TBADEDC, it is essentially incapable of solubilizing other sodium cation electrolytes such as sodium trifluoromethane sulfonate (NaTFMS) or sodium iodide. In fact, the ionic conductivities of TETD solutions with added NaI or NaTFMS show that if these salts are dissolved at all, they are totally undissociated, possibly due to insufficient polarizability of the I^- and $TFMS^-$ anions. It is also interesting to note that the equivalent conductivities of the two reduced salts of TETD (NaDEDC and TBADEDC) were approximately equivalent, and both were higher than the equivalent conductivity of a similar dithiocarbamate, NaDMDC. This implies that TETD is either better at dissociating electrolytes with a DEDC anion, or that the mobility of the DEDC anion is higher in the TETD melt than that of other dithiocarbamate anions. It has been previously

suggested that large organic ions cause substantial disruption of solvent structure with resultant lowering of local viscosity (11), therefore predicting a higher mobility of the large DEDC anion.

The encouraging results from the introduction of TCNQ into the TETD melt are also included in Table 2. It is well known that TCNQ and TCNE form charge-transfer complexes with disulfides; TCNQ is probably best known for the charge-transfer complex formed with tetrathiafulvalene, an organic metal (12,13). TCNE has been used in the sulfur electrode of sodium/sulfur batteries resulting in higher charge acceptance, although the reasons given for increased are rather unclear (14). TCNE and TCNQ were added to separate samples of TETD. The visual evidence for complex formation was striking; upon mixing the solids at room temperature the TETD crystals immediately darkened, and after heating TETD above 74°C the melts in both cases turned jet black, indicating the formation of a charge-transfer complex.

The observed conductivity of the TETD melt increased substantially from 10^{-7} to 10^{-6} (ohm cm)$^{-1}$ at 130°C due to the addition of 0.5 wt% TCNQ. This increase in conductivity is probably due to an increase in ionic transport in the melt and/or due to a substantial decrease in melt viscosity (15). It is well known that cyanide ion can attack thiuram disulfides to yield thiocyanate and the thiuram monosulfide (16). However, in table 2 it can be seen that the conductivity of 0.63M NaDEDC is approximately 3 times greater than that of 0.05 M TCNQ while it is 12 times as concentrated, so that the conductivity of TCNQ is essentially 4 times greater per mole added to the melt, a remarkable effect if only due to ionic transport. Evidence of chemical degradation of the TETD melt by addition of TCNE included gas evolution was observed at 130°C; however, no such degradation was observed with TCNQ. Additional evidence of irreversible chemical reaction with these compounds includes hysteresis of the conductivity on cooling; after cycling the melt to a higher temperature the lower temperature conductivity had increased. Certainly, additional studies are needed to elucidate the nature of the large conductivity increases observed with TCNQ and TCNE since they may

prove quite useful in lowering the resistivity of organosulfur melts.

CONCLUSIONS

The ionic conductivity of the TETD electrode increases by 3 orders of magnitude in going from the neat melt to about 10 % discharge composition of a Na/TETD battery. The equivalent conductivity of the NaDEDC/TETD melts implies significant ion pairing and formation of triplet ions which is expected for electrolytes dissolved in a solvents of low dielectric constant. The low values of equivalent conductivity in TETD are also explained by the high measured values of viscosity leading to low ion mobilities. As a solvent TETD appears to be very effective at dissolving salts having the dithiocarbamate anion, but quite ineffective at dissolving other strong electrolytes. The addition of TCNQ and TCNE to the TETD melts strongly increased the conductivity of the melts, but the nature of that increase requires further study.

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FIGURE CAPTIONS

Figure 1. The ionic conductivity of NaDEDC dissolved in pure molten TETD at 130°C as a function of concentration of the electrolyte.

Figure 2. The equivalent conductivity of NaDEDC in TETD as a function of $(\text{concentration})^{1/2}$ at 130°C; -·-·-·- expected behavior at dilute concentrations; ····· effect on equivalent conductance by the addition of the solvent tetramethylurea.

Figure 3. The equivalent conductivity of NaDEDC dissolved in DMSO as a function of $(\text{concentration})^{1/2}$ at 20°C.

Figure 4. The equivalent conductivity of NaDEDC dissolved in diglyme as a function of $(\text{concentration})^{1/2}$ at 20°C.

Figure 5. Arrhenius plot of the viscosity of molten TETD.

Figure 6. Arrhenius plot of the ionic conductivity of 0.5 M NaDEDC dissolved in molten TETD.

Figure 7. Arrhenius plot of the ionic conductivity of 6.2 M NaDEDC dissolved in diglyme.

Table 1

Concentration (mol/l)	Conductivity $(ohm\ cm)^{-1}$ Temp. = 130°C	Equivalent Conductivity $(ohm^{-1} cm^{2} equiv^{-1})$
0.0379	3.02×10^{-6}	0.079
0.0754	6.75×10^{-6}	0.0895
0.113	8.94×10^{-6}	0.0791
0.186	2.08×10^{-5}	0.118
0.329	4.26×10^{-5}	0.129
1.536	2.46×10^{-4}	0.160
2.442	5.23×10^{-4}	0.214
3.751	9.86×10^{-4}	0.263
3.337*	1.02×10^{-3}	0.306

*10% tetramethyl urea added

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Table 2

Electrolyte	Concentration	Solvent	CONDUCTIVITY (ohm cm)$^{-1}$ 100°C	130°C	E_a (kcal/mol)
TETD	Neat	TETD	6.0×10^{-8}	2.3×10^{-7}	5.8
NaDEDC	0.63	TETD	1.6×10^{-5}	8.0×10^{-5}	6.4
NaDMDC	0.76	TETD	1.6×10^{-6}	1.2×10^{-5}	8.0
TBA DEDC	0.13	TETD	8.0×10^{-6}	5.6×10^{-5}	
NaI	(1.0)*	TETD	4.4×10^{-8}	3.0×10^{-7}	
NaTFMS	(0.76)*	TETD	5.2×10^{-8}	2.4×10^{-7}	
TCNQ	0.05	TETD	4.3×10^{-6}	2.7×10^{-5}	
NaDEDC	0.94	DMSO	(4.6×10^{-3})**		
NaDEDC	0.94	Diglyme	(2.7×10^{-5})**		

* Very little of salt in solution

** Temperature = 20°C

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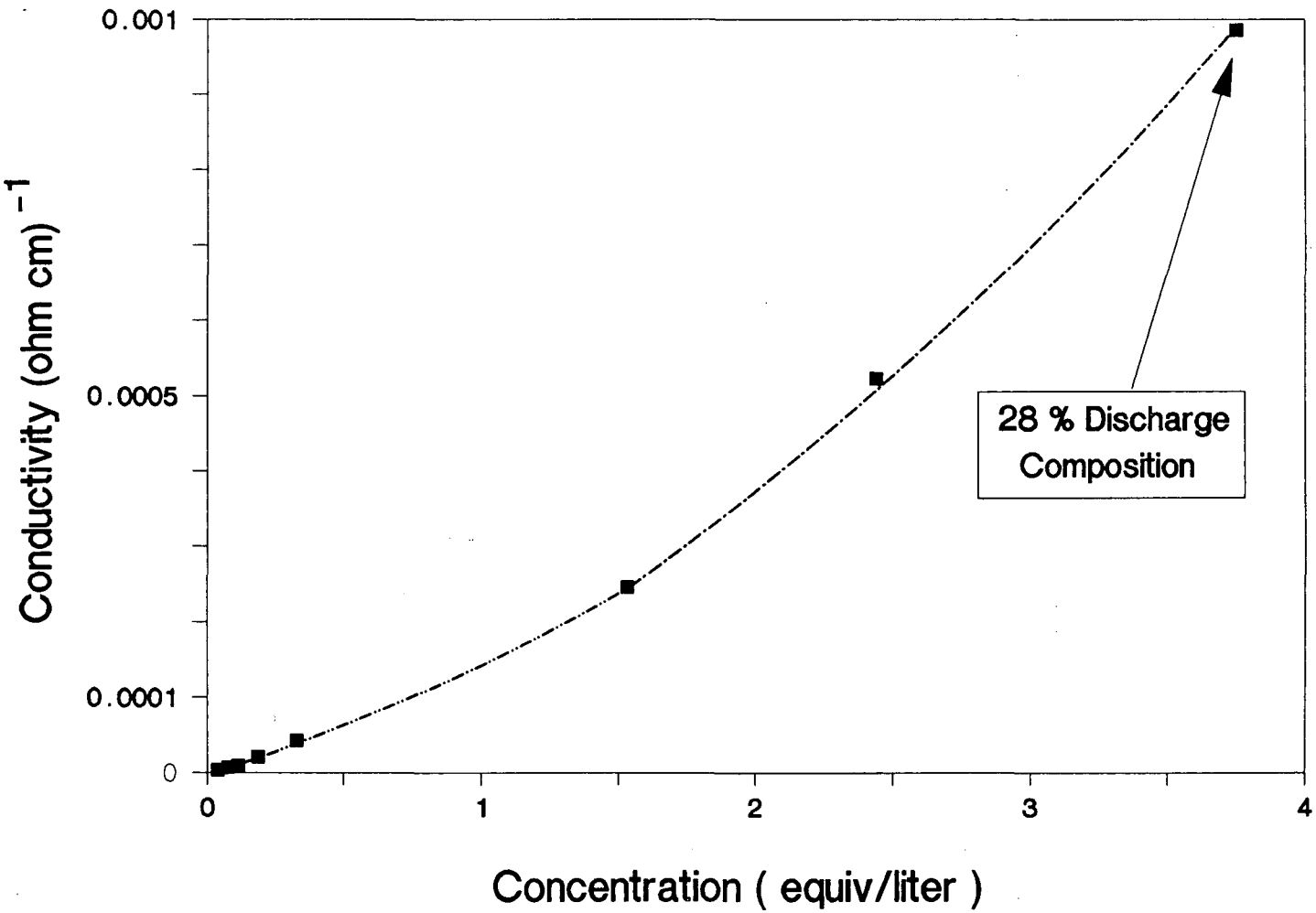

Fig. 1

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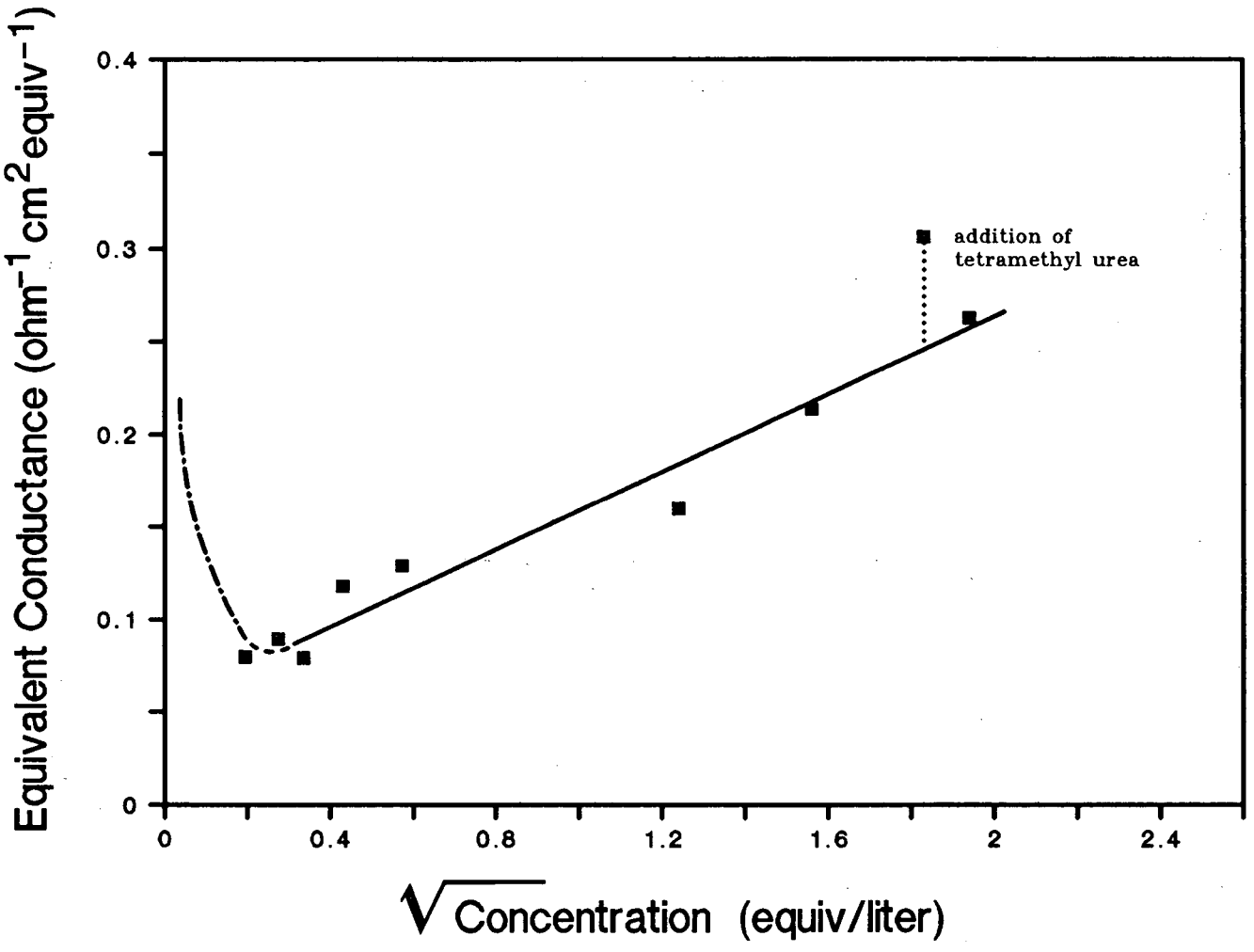

Fig. 2

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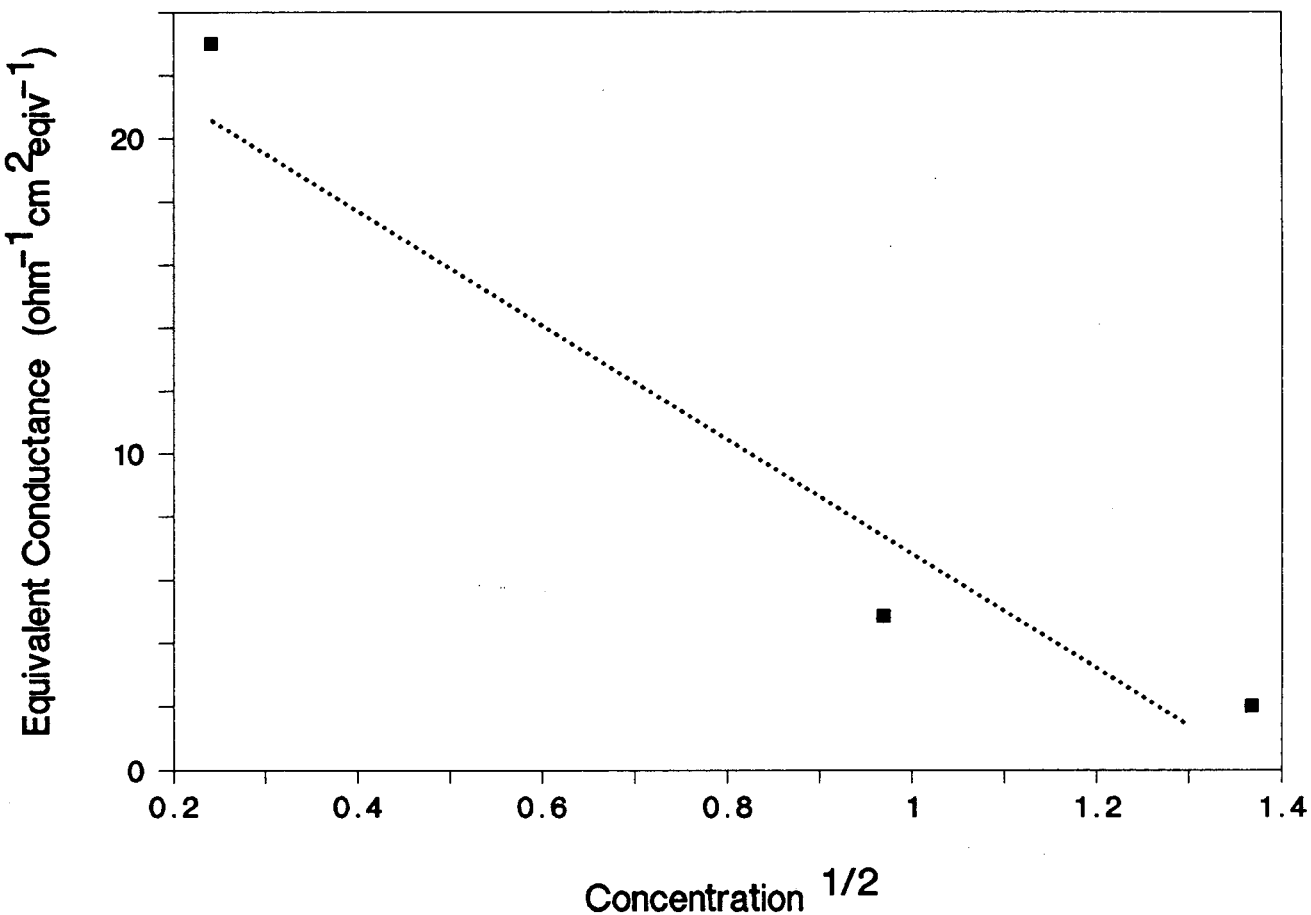

Fig. 3

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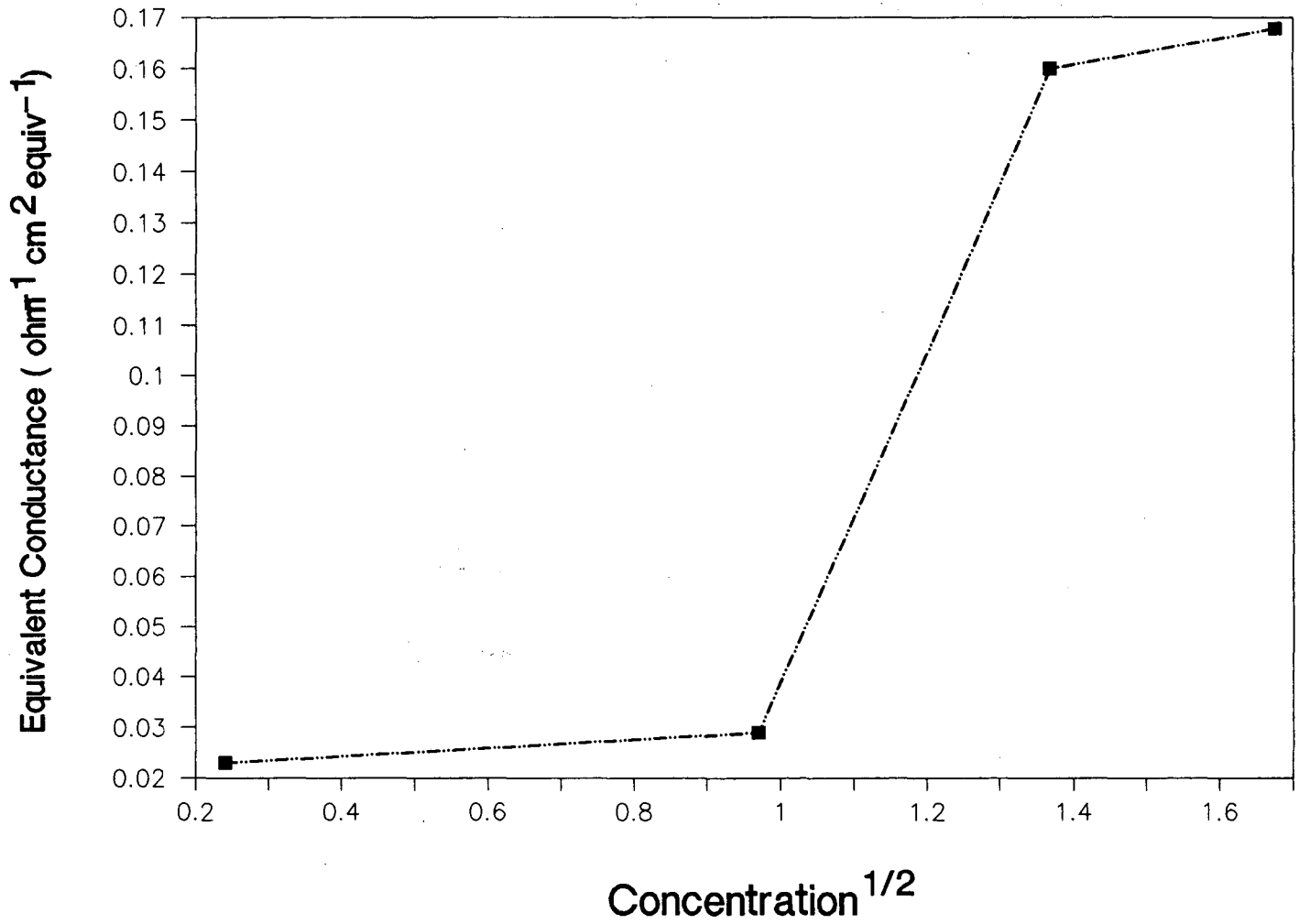

Fig. 4

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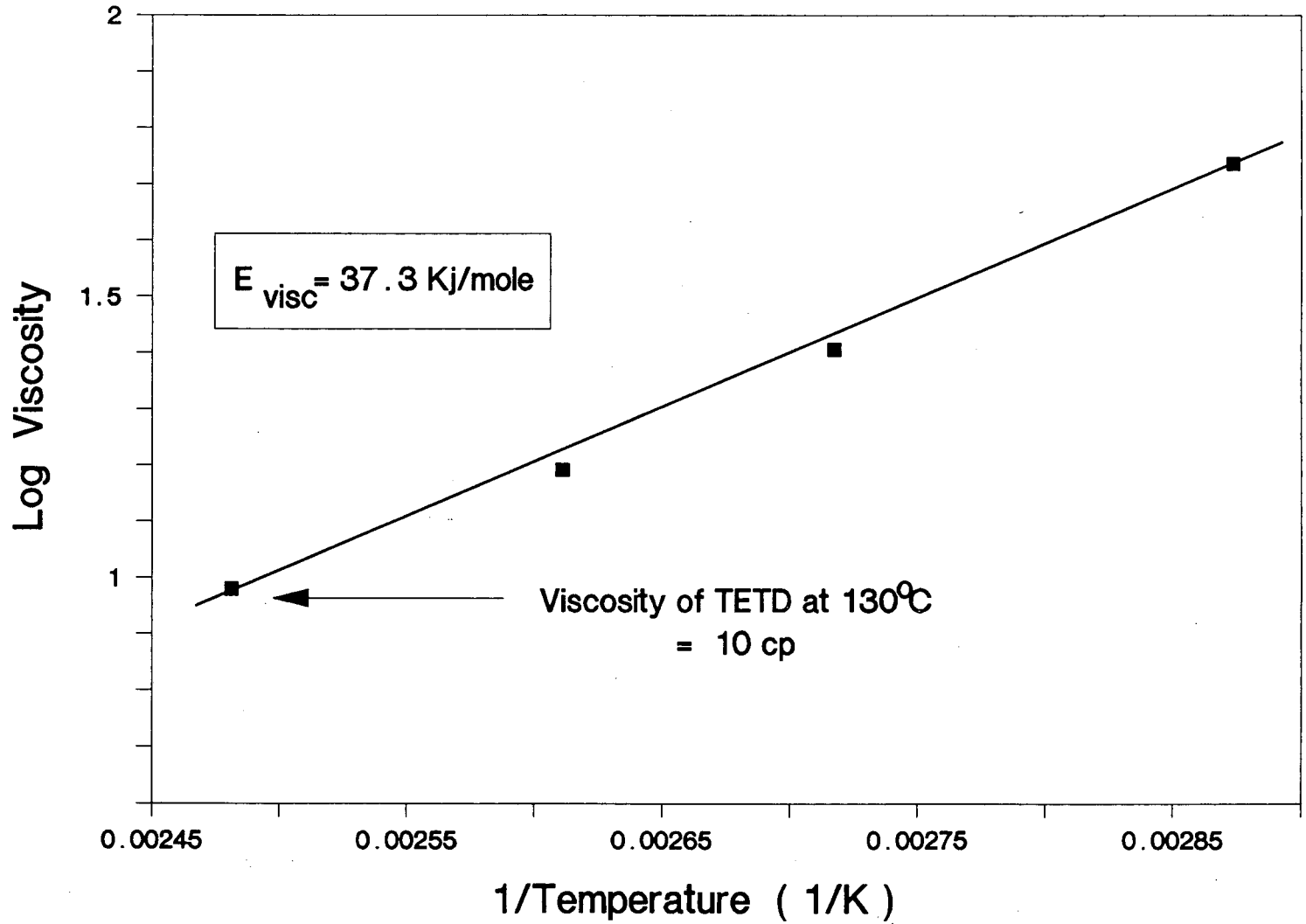

Fig. 5

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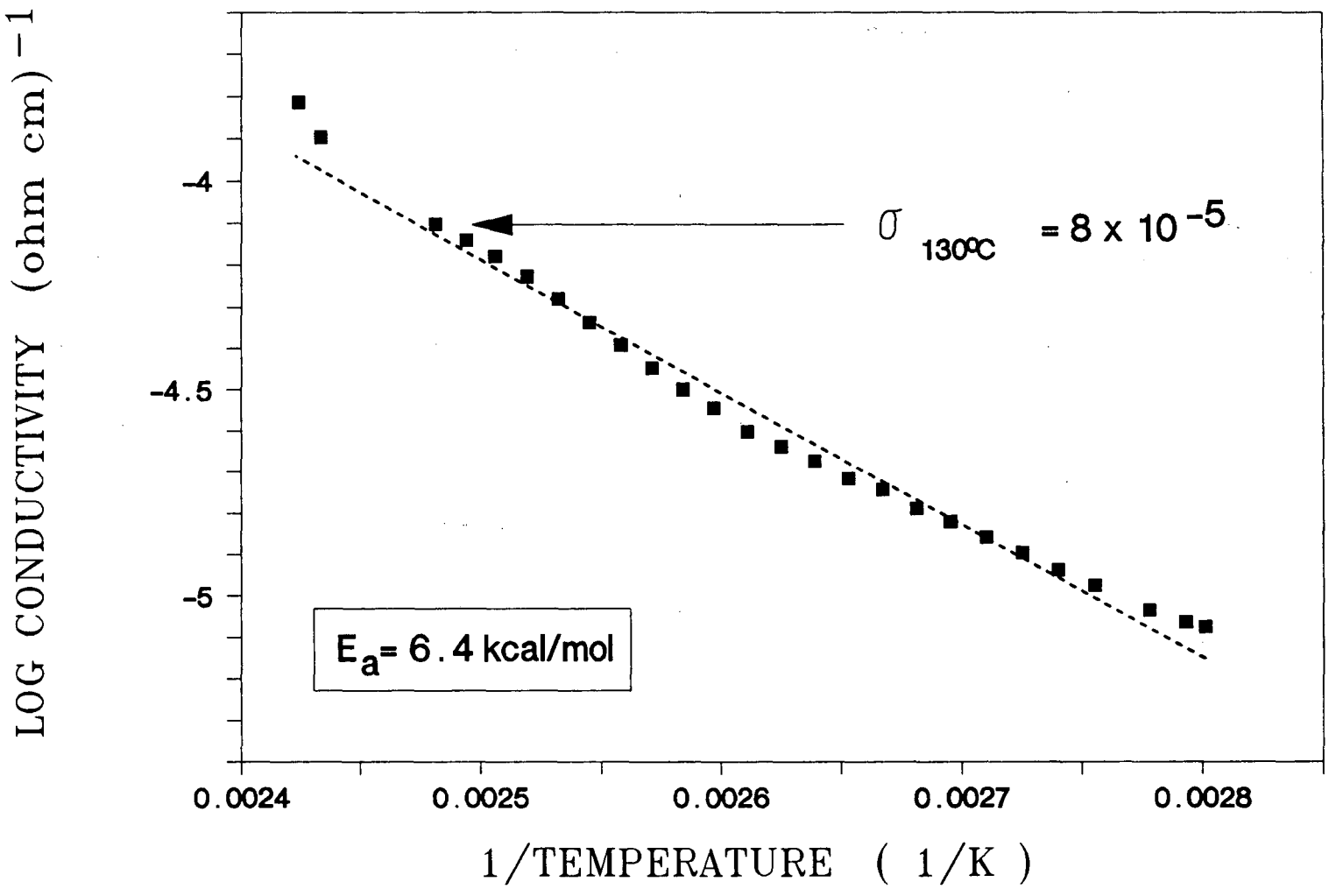

Fig. 6

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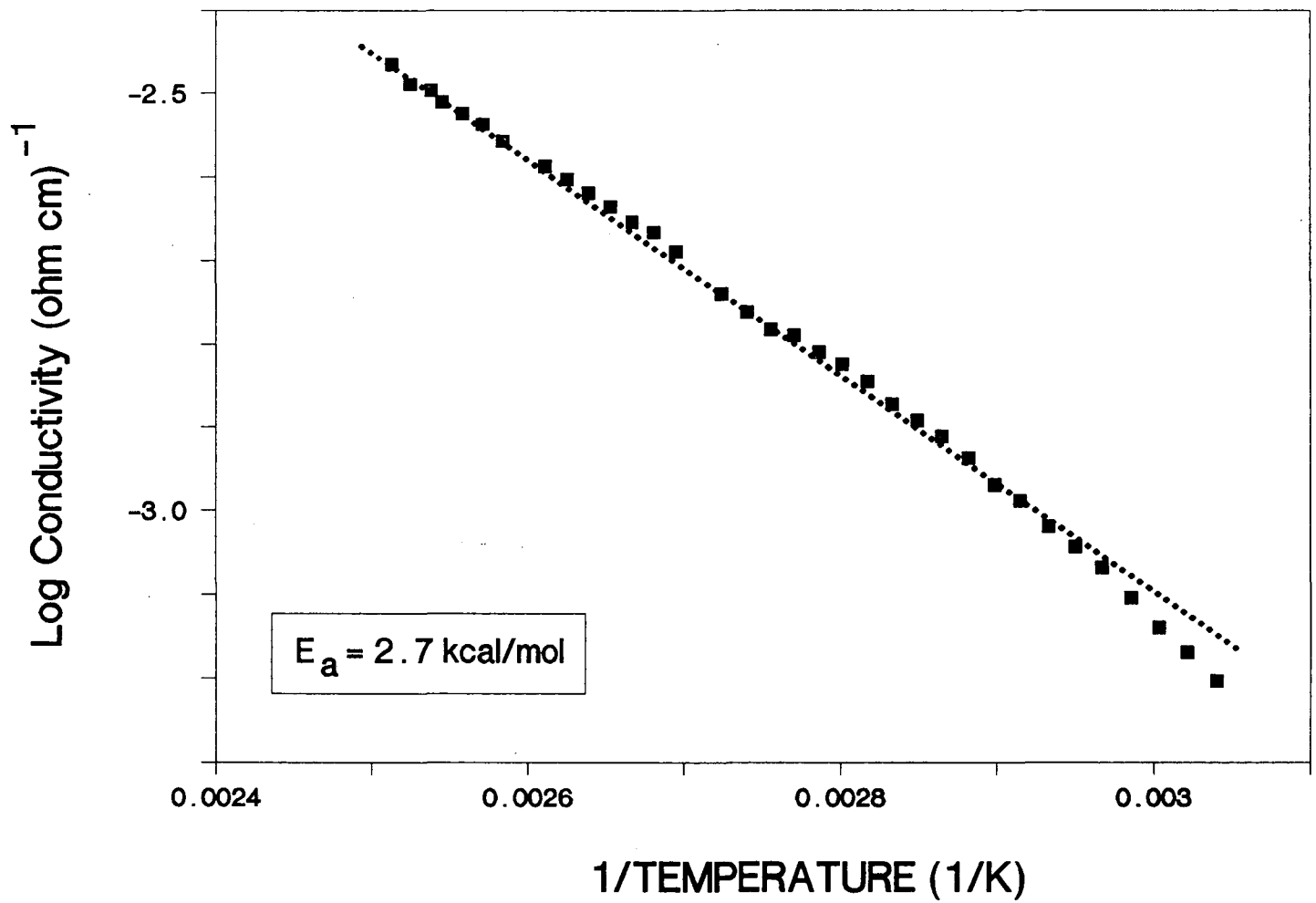

Fig. 7

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