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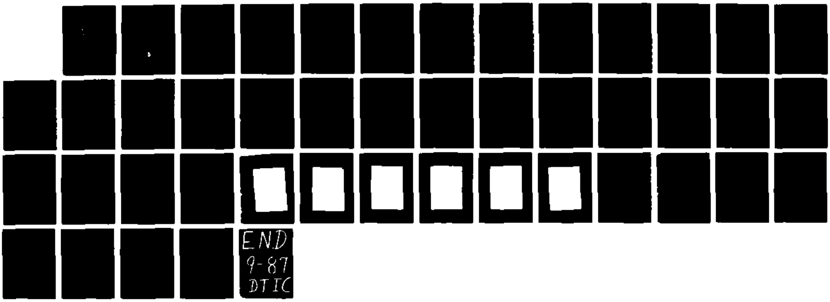

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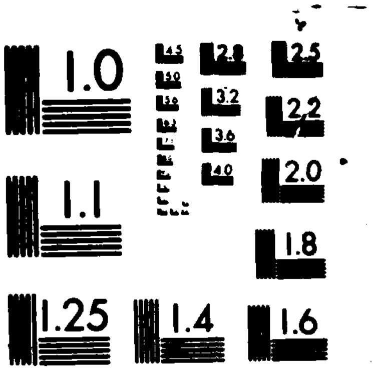
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Enantioselective Redox Transformations at Electrodes Modified with Cholesteric Liquid Crystals

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Enantioselective Redox Transformations at Electrodes Modified with Cholesteric Liquid Crystals

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Abstract:

The electrochemical response of the resolved forms of tris(2,2′-bipyridyl) ruthenium (II/III) $\{Ru(bpy)_3^{3+/2+}\}$ was examined at electrodes modified with a cholesteric liquid crystal. Films of cholesteryl oleyl carbonate were cast from solutions in a variety of solvents onto glassy carbon or platinum electrodes by spraying with an air-brush, by spin-coating, and by dropping from a μ-syringe. At times, polyvinyl pyridine was incorporated to increase the viscosity of the film. Cyclic voltammetry was performed in water and acetonitrile. In the case of the aqueous electrolyte, both achiral and chiral salts were employed to assess their effect. The best results are demonstrated for the films which were sprayed on and subsequently examined using aqueous achiral electrolytes. The ratio for discrimination of one enantiomer vs. the other is 0.78. Films were also characterized microscopically before and after the electrochemical experiment. In a preliminary fashion, effects of the temperature and of the potential perturbation profile (triangular, square and sine) were explored.

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* Electrochemical Society Active Member

Introduction

In previous communications [1,2], we demonstrated the electrochemical behaviour of redox couples in bulk nematic liquid crystal (LC) solvents and in polymer-modified electrodes doped with LCs. In fact, the observation of order at the interface (viz. substantial differences in current response based on homeotropic vs. homogeneous alignment) prompted our further investigation of more delicate issues, e.g. the extent of order immediately adjacent to the electrode surface. While pursuing these issues, our work [2] and that of Oyama and others [3] steered us toward modifying an electrode with a cholesteric LC film. Since cholesteric LCs exhibit 'form' optical activity [4] (see below), we employed them with the hope of preparing an electrochemical interface with some enantioselectivity.

Stereoselective electron transfer in solution [5-9] and in interfacial processes [10-14] is receiving increasingly more attention. Central to these efforts is the design of chemical systems which allow structural differences in reactant/substrate to influence the ratio of products for which more than one diastereomeric possibility exists. Our interest in stereoselective electron transfer stems from experience with electrochemistry using liquid crystals as solvents and using modified electrodes for analysis and catalysis. In particular, our approach bridged these arenas by casting films of a cholesteric LC on electrodes.

Numerous general accounts of liquid crystal phases (mesophases) exist [15-17]. Cholesteric LCs, specifically, are oriented about an arbitrary director (with some thermal distribution) in a given molecular plane (Fig. 1). Above and below this plane, on an axis perpendicular to it, the director twists with some rotatory power which is characteristic of the sample and temperature. (These remarks and Figure 1 illustrate form optical activity.) Specific rotations for these materials are characteristically thousands of degrees for short (~1mm) path lengths and are difficult to measure. The distance traversed along the helical axis before the director rotates upon itself is termed the pitch or spatial period, $2\pi/q_o$. (Note that despite the polarity along the long axis of these molecules, heads and tails are macroscopically indistinguishable.) Furthermore, the sense of rotation has a certain handedness which does not allow the existence of a simple enantiomeric pair. When the pitch corresponds to optical wavelengths, selective light reflection occurs [16]. This feature of cholesterics may be exploited in thermography by applying them as films [18].

We report the electrochemical and microscopic characterization of films of cholesteryl oleyl carbonate (COC) on electrodes to investigate possible enantioselectivity. Current responses for the resolved forms of the redox couple tris(bipyridyl)ruthenium (II/III) ($Ru(bpy)_3^{3+/2+}$) were the criteria used to determine the existence of enantioselectivity. Different methods of casting the films as well as different solvents, electrolytes, and electrode materials were examined. In addition, temperature effects were explored in a preliminary fashion.

EXPERIMENTAL

Instrumentation

A Pine RDE3 potentiostat and a Soltec VP6423S XY recorder were employed for cyclic voltammetry in a one-compartment cell. All potentials reported are versus the sodium saturated calomel electrode (SSCE), neglecting any junction potential. Working electrodes, Pt and glassy carbon, were mounted in KEL-F (BAS Corp.). A Pt wire was used as the auxiliary electrode.

Pre-treatment of the working electrode entailed rinsing with H_2O, acetone; sonicating in $MeCl_2$; rinsing with acetone; polishing; rinsing with H_2O, acetone; sonicating in acetone; rinsing with acetone; and blotting with a Kimwipe. It was polished with Metadi (6μ) diamond paste (Buehler) on a Micro cloth (Beuhler). In some cases ACM-72 (Atomergic) was subsequently applied to the electrode, according to the manufacturer's directions, aiming to establish the planar orientation .

Optical activity measurements were obtained with a Perkin Elmer 241 polarimeter using a 1 mL quartz cell. Ultraviolet-visible absorption spectra were obtained with a Hewlett-Packard 8451A Diode Array Spectrophotometer.

Films of the cholesteric LC were applied by three different methods. In the first case, a solution of COC (Pressure Chemical Co.) in methylene chloride ($MeCl_2$) was dropped onto the inverted working electrode from a microsyringe (Hamilton). Secondly, films were cast from a solution of COC in $MeCl_2$ using a Badger 350 Air

Brush Set. A brass fitting was made to connect the air brush to a tank cylinder of pre-purified nitrogen which allowed accurate and reproducible deliveries. Finally, films were spin-coated onto the working electrode by mounting the electrode in an ENCO Model 40030 drill press. A solution containing COC in $MeCl_2$, hexane, or acetonitrile (MeCN) was brought into contact with the electrode and removed, allowing the solvent to evaporate while the electrode rotated.

Films were examined and photographed with a Nikon Optiphot microscope (reflected light) and a Nikon FG camera. Slides of representative areas of the working electrode greatly facilitated comparison of the films: one film to another; and the film before and after the electrochemical experiment.

Reagents

All reagents were used as received, except where noted. Water was passed through a three-stage purification train (Hydro Systems or Milli-Q). Potassium perchlorate (GFS) was recrystallized three times from boiling water and vacuum-dried at 90°C for 72 hours. Tetrabutylammonium perchlorate (GFS) was hot-filtered, recrystallized three times from ethyl acetate, and vacuum-dried at 90°C for 72 hours.

R(-) 10-camphor sulfonic acid, ammonium salt (Aldrich) was recrystallized twice from ethanol and vacuum-dried at 82°C for 48 hours. (See Table I for specific rotations of compounds used in the preparation of optically active electrolytes.) S(+) 10-camphor sulfonic acid (Aldrich) was recrystallized twice from ethyl acetate and vacuum-dried at 82°C for 48 hours.

The methylated iodides of R,R(-) and S,S(+) 2,3 dimethoxy bis 1,4 dimethyl amino butane (Aldrich) were prepared as follows. The reaction flask was charged with 5.00g (24.5 mmol) of the R,R(-) diammine and 100 mL methanol, and the solution was stirred for one hour under a stream of nitrogen. At least 9 mL (145 mmol) of freshly distilled methyl iodide (Aldrich, 40-41°C fraction) were added to the flask with a back-pressure of nitrogen. The solution was refluxed under nitrogen for at least 12 hours. Some precipitate appeared during the course of the reaction. The mixture was cooled to room temperature, and ethyl ether was added dropwise until further addition gave no turbidity. The mixture was cooled to -10°C, filtered, and washed with ethyl ether, giving 10.69g (21.9 mmol, 90%) of crude product with a faint yellow color.

The whole amount was dissolved in a minimum of boiling methanol and hot-filtered from activated charcoal (Norit). Subsequently it was recrystallized twice from methanol/ethyl ether: ^1H NMR (D_2O, Aldrich) δ3.26 (s, 9H), 3.4-3.7 [overlapping patterns] (m, 5H), 4.38 (broad d, 1H).

Some difficulty was encountered in the metathesis of the chiral cation (2,3 dimethoxy bis 1,4 trimethylammonium butane) / chiral anion (10-camphor sulfonic acid) salt. (For simplicity, we will refer to these salts by their absolute configuration with a dash between cation and anion, e.g. S,S-S.) Since no solvent was found which isolated the chiral cation/chiral anion pair, and since the precursor salts were together soluble in water at one-tenth molar, solutions of these salts were isolated by ion-exchange.

Amberlite CG-120* Type 2 (Fisher, strong cation exchange resin, 0.80g) was poured as a slurry into a 10mL buret. The course of the ion-exchange process was followed by pH measurement, visible absorption spectrophotometry (aqueous solutions of 10-camphor sulfonic acid exhibit a peak in their absorption spectra at 286 nm), or both, as appropriate. The total number of milliequivalents in the column was 3.44 by determination (3.4 by calculation from the manufacturer's data).

The column was loaded with a solution containing the diiodide salt of the chiral cation at 0.153N. The column was washed with water until the washings showed no trace of iodide, as determined by addition of a few drops of 0.1M silver nitrate. The chiral cation was then eluted with the ammonium salt (or acid) of the chiral anion at 0.1M. Three solutions were isolated in this way. The observed and calculated specific rotations are given in Table II. Cyclic voltammetry was performed on each of these solutions over the potential range of interest; a representative background current scan is given in Figure 2.

Dipotassium L-tartrate was prepared by dropwise addition of an aqueous solution of potassium hydroxide (Mallinckrodt) to an aqueous mixture of L-tartaric acid (Aldrich, Gold Label) in an ice bath until the pH was greater than 10. The resulting solution was evaporated to crystallization, cooled in an ice bath, and filtered in two crops. The combined filtrate was recrystallized from water.

Tris(bipyridyl)ruthenium perchlorate hexahydrate was resolved by aspirating to crystallization (with subsequent filtration) an aqueous solution (60 mL) of $Ru(bpy)_3Cl_2*6H_2O$ (Strem Chemicals, 1.26g) and dipotassium L-tartrate (29g) to obtain the diastereomers in eight portions. Each of the eight portions was dissolved in a minimum of water to which solution was added aqueous sodium perchlorate (GFS, 0.6g/mL), precipitating the perchlorate salt. Each of the eight portions was examined for optical activity; two portions showed high optical purity.

The dextro salt thus isolated gave $[\alpha]_D^{21}=+859°$, c=0.060 (op= 105% [19]). The laevo salt gave $[\alpha]_D^{21}=-776°$, c=0.014 (op= 95%).

Polyvinylpyridine (Polysciences, lot #2 1693) was purified by dissolving it in methylene chloride and by dropwise addition of the solution into ethyl ether which was vigorously stirred. The color of the resulting precipitate improved from a pale yellow to a bright white. Some films were cast from solutions incorporating PVP, the goal being stabilization of the films properties by increasing its viscosity.

Results and Discussion

The number of variables addressable necessitated, at least initially, an empirical approach. In the casting of the film one may vary electrode pre-treatment, the cholesteric LC, the method of casting, the solvent, the concentration, or the presence absence of stabilizing agent. Also one can envision post-treatment (e.g. temperature/potential excursions) of the modified electrode prior to electrochemical analysis. During the electrochemical experiment, one may vary the electroactive component, solvent, electrolyte, or temperature.

We chose cholesteryl oleyl carbonate (Fig. 3) because it has a cholesteric phase at room temperature [20]. On heating, COC passes monotropically from the crystal to the cholesteric phase at 26.7°C and then to the isotropic liquid at 34°C. The cholesteric phase supercools at 20°C to give the smectic phase.

Electrochemistry at films of COC on electrodes, as opposed to the bulk COC, was pursued primarily because of the low dielectric constants typical of organics which would give rise to a poor electrochemical response [1]. Furthermore, it is much easier to examine the microscopic appearance or 'texture' of a film rather than a cumbersome bulk sample. (Of course, dramatic differences may exist for the electrochemical behaviour between the two media.)

The textures (e.g. Figs. 5a-f) of cholesteric LCs are typically planar, where one looks down the optic axis (gray field for crossed polars),or focal conic, where the optic axis is parallel to the field of view (high contrast black and white, birefringent, for crossed polars) [21]. The optic axis is the helical axis of rotation. We believe the establishment and preservation of the planar texture at the interface will show the most chiral discrimination. This point may be clarified by considering the various contributions to the current response.

Treating diffusion as an activation controlled process, one may regard the transition states for a pair of enantiomers in a chiral medium as diastereotopic. Diffusion for the enantiomer which is more-conforming to the form optical activity of the cholesteric LC will be retarded more than the less-conforming enantiomer. Moreover, diffusion in keeping with form optical activity occurs along the helical axis. By comparison, differences in transition states for a pair of enantiomers diffusing inclined or perpendicular to the helical axis are small, because a given enantiomer will 'see' only ordinary (molecule-based) optical activity.

The above considerations illustrate that an electrode with the planar texture should exhibit the most chiral discrimination manifested in the current. Another contribution to the current may be cited. Ionic motion of achiral electrolyte resulting from double-layer charging may (and probably does) give rise to non-selective channels in the film, enabling diffusion which will show no chiral discrimination.

The electroactive components throughout this communication are the resolved forms of $Ru(bpy)_3(ClO_4)_2{*}6H_2O$. The $Ru(bpy)_3$ II/III couple was chosen because it is electrochemically reversible and because oxidation of the dication with subsequent reduction proceeds with configuration retention, i.e. it does not racemize [19].

During the course of the electrochemical experiments, the concentration of the ruthenium complex was checked and rechecked by visible absorption spectrophotometry and by voltammetry at a bare electrode. Typically, voltammograms were obtained at three scan rates (50, 100, and 150 mV/s) for a given film. The peak currents measured were plotted versus the square root of the scan rates. The slopes of these lines, corrected for electrode area and concentration, are presented in Tables III-VI. The stability of each COC film was demonstrated by obtaining a voltammogram at 50 mV/s at the beginning and end of any electrochemical experiment. Comparing the per cent difference of the peak currents for these two scans gave an average of 2.7% with a standard deviation of 2.0%.

Films Prepared with a μ-Syringe

Initial attempts at preparing films which discriminate on the basis of chirality were done using a μ-syringe by dropping between 1.4 and 3 μL of solution onto a glassy carbon electrode. At least 1.4 μL was necessary to cover the entire surface with a drop. Neat methylene chloride was dropped onto the surface to ensure it was level. Applications of COC followed with treatment of the electrode and the co-presence of polyvinylpyridine in solution as variables.

The rate and number of applications was typically 2 μL four times. The concentration of COC in $MeCl_2$ was 6.7 mg/mL. Alternatively, a solution of COC (6.7mg/mL) and PVP (0.58mg/mL) was applied.

Pre-treatment of the surface was effected several times with ACM-72 in an attempt to achieve a monodomain in the first monolayer of coverage. The incipient film however diminished the current response severely enough to warrant discontinuing its use altogether.

Throughout all these efforts, differences in the current response for the resolved forms of $Ru(bpy)_3^{3+/2+}$ in aqueous KNO_3 (0.1M) were not observed.

Films Prepared by Spin-Coating

The rotation rate was varied between 250-3600 rpm. Methylene chloride, acetonitrile, and hexane were all tried as solvent from which to cast the films. The concentration of COC ranged from 16 mg/mL to 70 mg/mL. Stabilization of the film with regard to viscosity was attempted with PVP at 3.6μg/mL. Voltammetry was tried in COC saturated MeCN/TBAP and aqueous $KClO_4$. The results for these trials were as disappointing as for the films prepared with the μ-syringe. They showed no selectivity outside the limits of error.

Films Prepared with Air Brush

Because of early successes with this method of application, it was the most avidly investigated. The operating pressure of the air brush was varied between 14-22 PSI. The concentration of

COC in $MeCl_2$ ranged from 0.4mg/mL to 10mg/mL in both the presence and absence of PVP whose concentration when present ranged from 3.6μg/mL to 8.9μg/mL. Application of the films varied from 1 to 5 coats with 6 to 10 passes of the air brush over the electrode per coat. The air brush was held between 4 and 5 inches from the surface. The electrolytes used included KNO_3/H_2O, $KClO_4/H_2O$, chiral salts/H_2O, and COC saturated acetonitrile/tetrabutyl ammonium perchlorate, all salts being at 0.1M. The electrochemistry in MeCN was pursued at glassy carbon and platinum electrodes.

By far the most discriminating films were cast at 14 PSI with 3 coats at 10 passes per coat using a solution of COC (9.1 mg/mL) and PVP (3.6μg/mL). A representative voltammogram is given in Figure 4 for a film on glassy carbon in aqueous $KClO_4$. Also shown is a voltammogram for native glassy carbon under otherwise identical conditions. Table III summarizes the results for aqueous electrolytes. (Note again that each entry in Tables III-VI represents at least four measurements appropriately normalized.)

At a bare electrode, the bulk current response of one enantiomer should be identical to its mirror-image (which is in contrast to the current response of a monolayer surface coverage [11]). Indeed, this is observed. In Table III, taking the average of the anodic slopes for each enantiomer at a bare electrode, and finding the percent difference of the two, one obtains 1.7%. This value is an estimate of the limit of error, since twenty measurements were taken to obtain it. Similarly, the percent difference of the anodic slopes for the two enantiomers in Tables IV and V are 2.4% and 1.7%, respectively. The percent difference of the cathodic slopes for the two enantiomers in Tables III-V are more disparate, ranging from 3.4% to 7.2%. This, however, can be attributed to the lower accuracy in drawing the base line for the cathodic wave (cf. anodic and cathodic counterparts of voltammogram in Fig. 4).

To demonstrate the existence of chiral discrimination, the data in Table III is analyzed as follows. The diminished anodic response for the (+) isomer at a film electrode is compared to its response at a bare electrode. This ratio, representing a reduction in signal, is compared to the corresponding ratio for the (-) isomer. Now this new ratio shows which enantiomer, if either, is retarded more. As it happens, averaging the results in Table III gives a ratio of 0.78, i.e., the (+) isomer is retarded by the film by a factor of 1/0.78 as compared to the (-) isomer. Note also that the cathodic slopes agree and that there is basically no difference between the two electrolytes listed.

In Tables IV and V results are presented for voltammetry in COC saturated MeCN / TBAP at platinum and glassy carbon electrodes. The discrimination is not as good as that in aqueous electrolytes, and that at glassy carbon is better than that at platinum. In fact, the above analysis gives a ratio of 0.89 for the case of glassy carbon, and a ratio of 0.97 for platinum. This ratio for platinum is barely outside the range of error.

The presence of optically active electrolyte was thought to influence enantioselectivity by minimizing non-selective channels (described earlier) in the film. The results portraying the discriminating ability of these films for three stereoisomers of a chiral cation / chiral anion pair are given in Table VI. (Note that any discrepancy in the purity of these electrolytes, as indicated in Table II, is solely the result of impurity in the cation, since the purity of the anion, the eluant, is confirmed in Table I.)

For each of the electrolytes in Table VI, the data at a <u>bare</u> electrode is at first glance intriguing. In the case of the R,R-R and S,S-S electrolytes, a difference in excess of the error limits exists for the anodic slopes of the (+) and (-) isomers. This observation may be understood in the following terms.

The inner and outer Helmhotz planes (IHP/OHP) for the R,R-R electrolyte / (+) isomer combination is diastereotopic to the IHP/ OHP for the R,R-R/(-) combination. This effect has been documented [10]. As such, they may, and do here, show different properties. Moreover, if the R,R-R/(+) combination shows higher limiting currents than the R,R-R(-) combination, the reverse situation should obtain for the S,S-S electrolyte. Indeed, this is observed as Table VI indicates. Consideration of Scheme I and Table VII further clarifies these observations.

In Scheme I, the relation of each electrolyte/enantiomer combination to all the other stereoisomers considered is given. Now the percent difference in the anodic slopes (averages) for each of the diastereomeric pairs (C-F in Table VII) is well beyond experimental error. Furthermore, the values listed cover quite a range, which is not unusual since the relationship they portray is diastereotopic. The crucial test, however, is the comparison of the two enatiomeric pairs (A and B in Table VII). Since enantiotopic states show no difference in properties, either enantiomeric pair should show no difference in limiting current behaviour, i.e., a percent difference within experimental error. As this is indeed the case, the results are internally consistent.

The question of the chiral cation versus the chiral anion being more influential in the compact layer still persists. It is addressed in the S,S-R/(+) and S,S-R/(-) combinations. Since the cation/anion pair of the electrolyte is mixed with respect to absolute configuration, its use allows one member of the ion pair (which one cannot be discerned here) to exert its stronger effect, should this be the case.

For example, if the chiral cation is more influential than the chiral anion toward establishing a diastereotopic compact layer, then the current responses for the (+) and (-) isomers will be different. If, on the other hand, neither cation nor anion is the more influential, the pair of combinations S,S-R/(+) and S,S-R/(-) will behave enantiotopically, despite the fact that they are diastereomers. The latter case is observed, as the data in Table VI for a bare electrode using the S,S-R electrolyte indicates.

What effect then do the films of COC on the electrode in conjunction with the chiral electrolytes have on the voltammetry?

In Table VI, a comparison of the reduction in response (ratio of film to bare electrode response) for the (+) and (-) isomers indicates no chiral discrimination for the film electrode. In fact, rather than the two effects (chiral electrolyte and cholesteric LC) being somehow additive, they appear to cancel each other. At this time no explanation is offered for this observation, and certainly these chiral electrolytes did not minimize any possible non-selective channels in the films, as planned.

Photographs of these films before and after electrochemistry revealed (to our surprise) no dramatic differences. Figures 5a-f serve to illustrate typically the differences for the various electrolytes and electrodes. Both the planar and focal conic textures are well illustrated in Figures 5a,e,f. The planar texture is represented by the areas showing interference-type fringes and having uniform color therein. The focal conic texture is represented by the birefringent areas, blue and orange patches. Enlargement in Figures 5e,f show that neither texture is 100% complete. In Figures 5b, d, and f, one may note that the film (after voltammetry) most uniform in the planar texture is the same as that giving the most chiral discrimination thus far, i.e., the film after voltammetry in the aqueous electrolyte, 5f. Also, the films on glassy carbon (Figs. 5a,b) appear significantly more organized than those on platinum (Figs. 5c,d), both before and after voltammetry in MeCN. This is remarkable in that films on platinum performed very poorly in comparison to those on glassy carbon.

An electrochemical cell has been fabricated to be used in conjunction with reflected-light microscopy, affording the in-situ monitoring of the films. (Details of its construction will be published at a later date.) By far, the greatest and most dramatic changes in the films, for acetonitrile or water, occured on contact with electrolyte or upon its evaporation. On the other hand, potential profiles (triangular, sinusoidal, and square wave) over a range of frequencies and amplitudes were applied resulting in faint or no change in appearance.

Temperature excursions to just below the isotropic clearing point (32°C) and to well above it (38°C) resulted in only mild changes in texture- typically the planar texture increased by 10-15% (i.e. 10-15% less birefringence). However, with regard to temperature excursions, only appearances were examined (not electrochemistry) in a before-and-after fashion, since the hot-stage being constructed and tuned is not completed. A more fundamental study of this phenomenon is in progress wherein the film's texture, temperature, history, etc. may be correlated with the degree of enantioselectivity.

Conclusions

The number of variables demonstrates that the work presented here is by no means exhaustive. We believe, however, that it is a preliminary undertaking of an area with bright prospects.

Attempts at preparing an electrochemical interface showing enantioselectivity were successful for two separate cases. For the case of films of cholesteryl oleyl carbonate on glassy carbon, the best results were obtained in aqueous electrolyte, the salt being achiral. Also, polyvinylpyridine acted to stabilize the films' properties by increasing the viscosity. It is possible that the acetonitrile electrolyte showed less chiral discrimination, as compared to the aqueous electrolyte, because of reorganization within the film as a result of swelling more.

For the second case, using chiral electrolytes at a bare electrode demonstrated a small measure of chiral discrimination. It is unclear at this time why the combined use of the chiral electrolyte and cholesteric LC did not effectively somehow add, but rather their combined use apparently canceled one another's effect altogether.

Reiterating that the approach taken was empirical, the cholesteric to nematic transition known to occur at high field strengths [16] is not discussed. This and other issues will be explored in an in-situ microscopic investigation of the electrochemical behaviour of these films.

Since favourable results were obtained in aqueous electrolytes, methanol, ethanol, and mixed solvents are appealing as candidates for further study. Electrochemical reactions of prochiral organic molecules (e.g. alkyl phenyl sulfides [14]) in these films should be very interesting since differences in transition state energies for the diffusion versus the reaction of diastereomers may be quite disparate. Other cholesteric LCs may prove dramatically more effective as a medium for stereoselective electron transfer. Also, surface-immobilized polymeric LCs may be a significant enhancement.

Finally, the roughness of the electrode surface may be a a deleterious factor. One may cast these films on a mercury pool electrode to address this issue.

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Figure Legends:

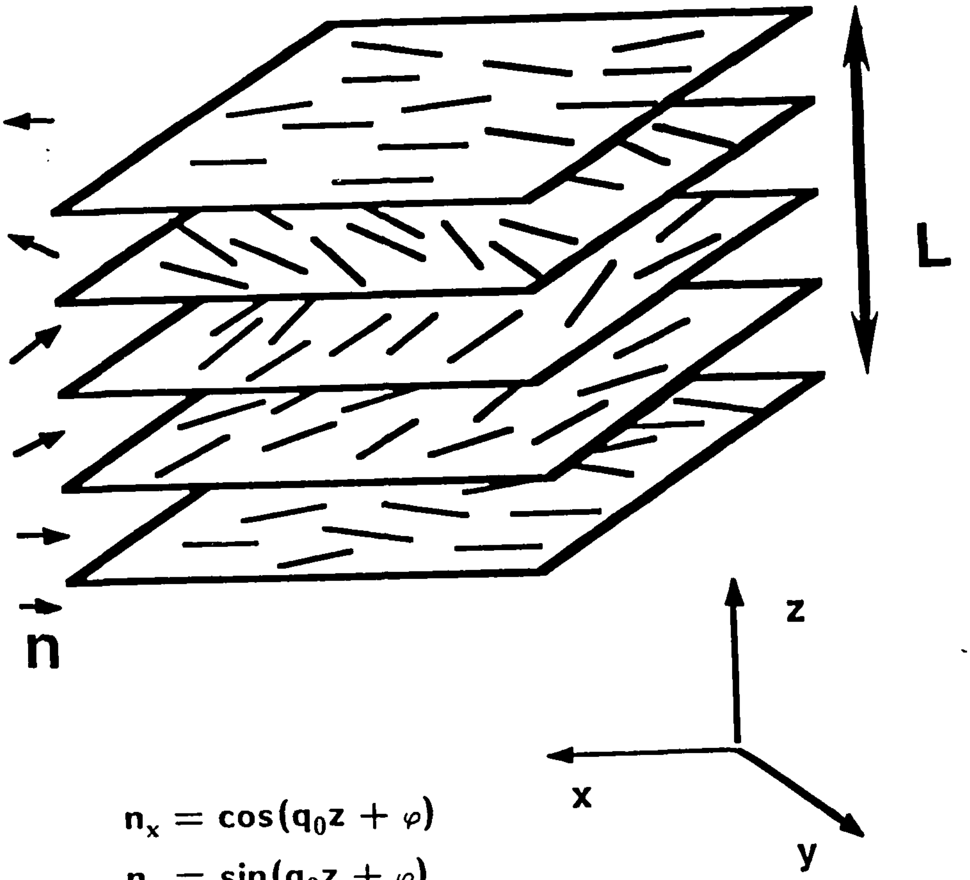
Figure 1. Schematic of a cholesteric liquid crystal, illustrating the pitch, L, and the local director, $\vec{n}$.

Figure 2. Cyclic voltammogram (background scan) at 50 mV/s of the electrolyte S,S-S isolated by ion-exchange.

Figure 3. Cholesteryl oleyl carbonate (COC) and its phases.

Figure 4. Cyclic voltammograms at 50 mV/s for a native glassy carbon electrode (solid curve) and a modified (see text) glassy carbon electrode (dashed curve).

Figure 5a-f. Representative photographs of films of COC on working electrodes, sprayed on using COC (9.1mg/mL) and PVP (3.6μg/ml) in $MeCl_2$. The arc in some of the photographs is where the electrode pellet meets the Kel-F. a) 20X, glassy carbon, before voltammetry; b) 20X, glassy carbon, after voltammetry in MeCN; c) 20X, Pt, before voltammetry; d) 20X, Pt, after voltammetry in MeCN; e) 160X, glassy carbon, before voltammetry; f) 80X, glassy carbon, after voltammetry in water. Photographs were taken with crossed polars and a first-order red tint plate using reflected light.



$$n_x = \cos(q_0 z + \varphi)$$

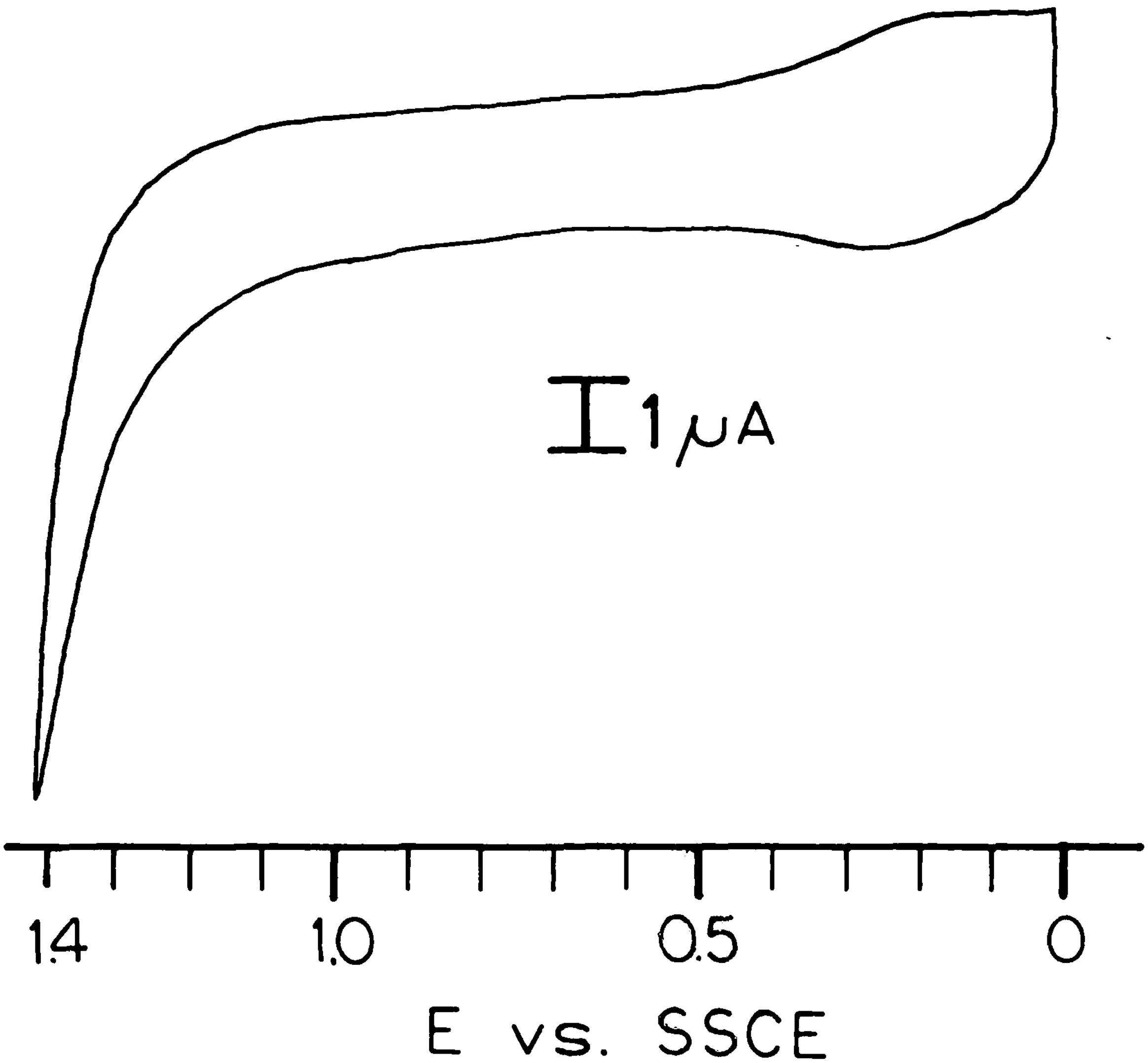
$$n_y = \sin(q_0 z + \varphi)$$

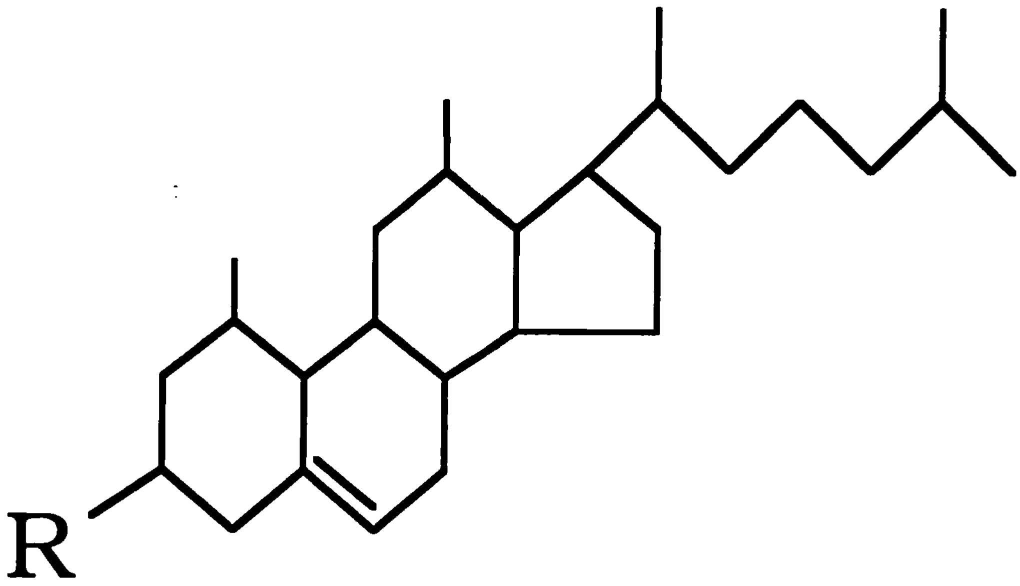
$$n_z = 0$$

$$L = \pi / q_0$$

FIG. 1

FIG. 2

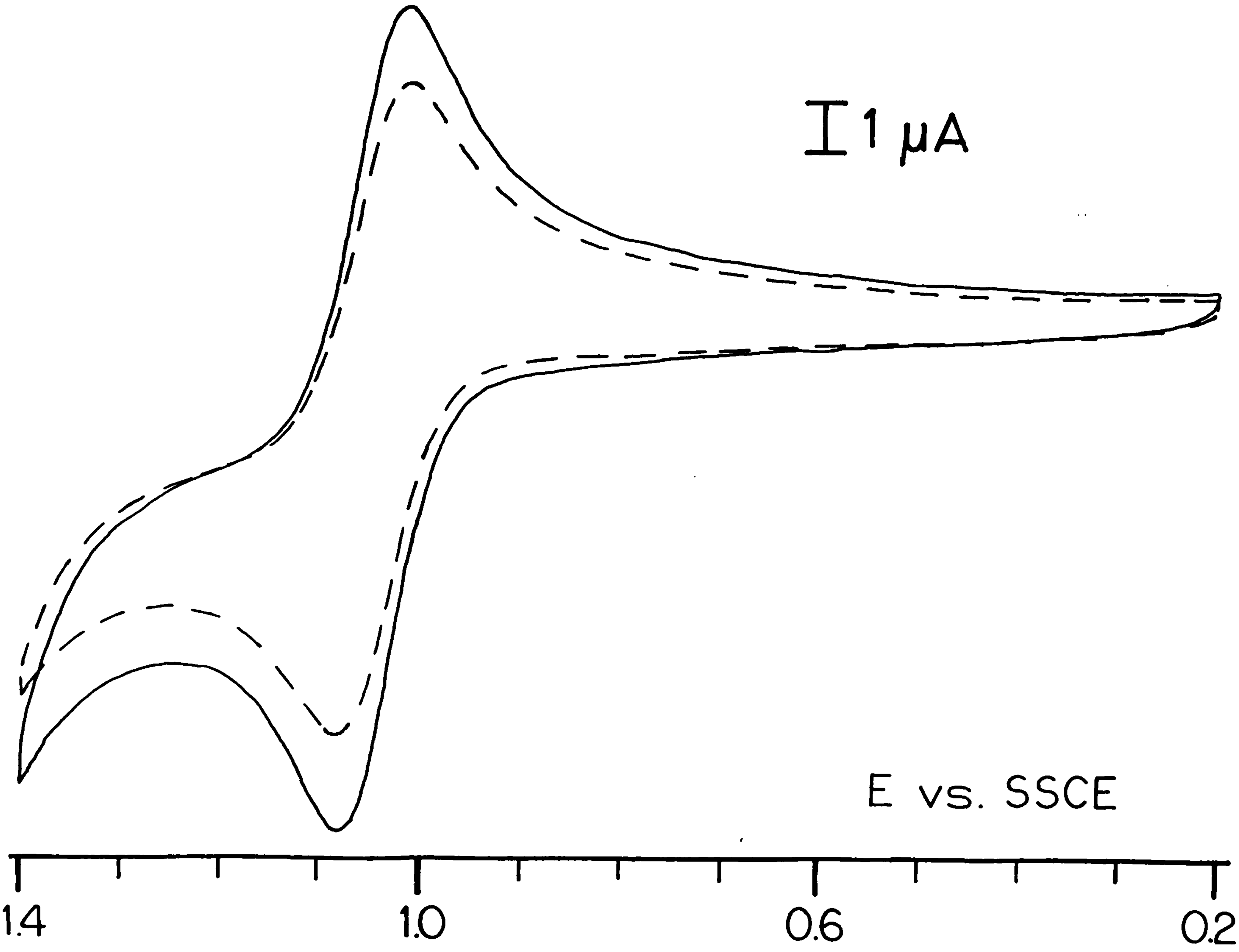




$R = CH_3(CH_2)_7CHCH(CH_2)_7OCOO-$

FIG. 3

FIG. 4



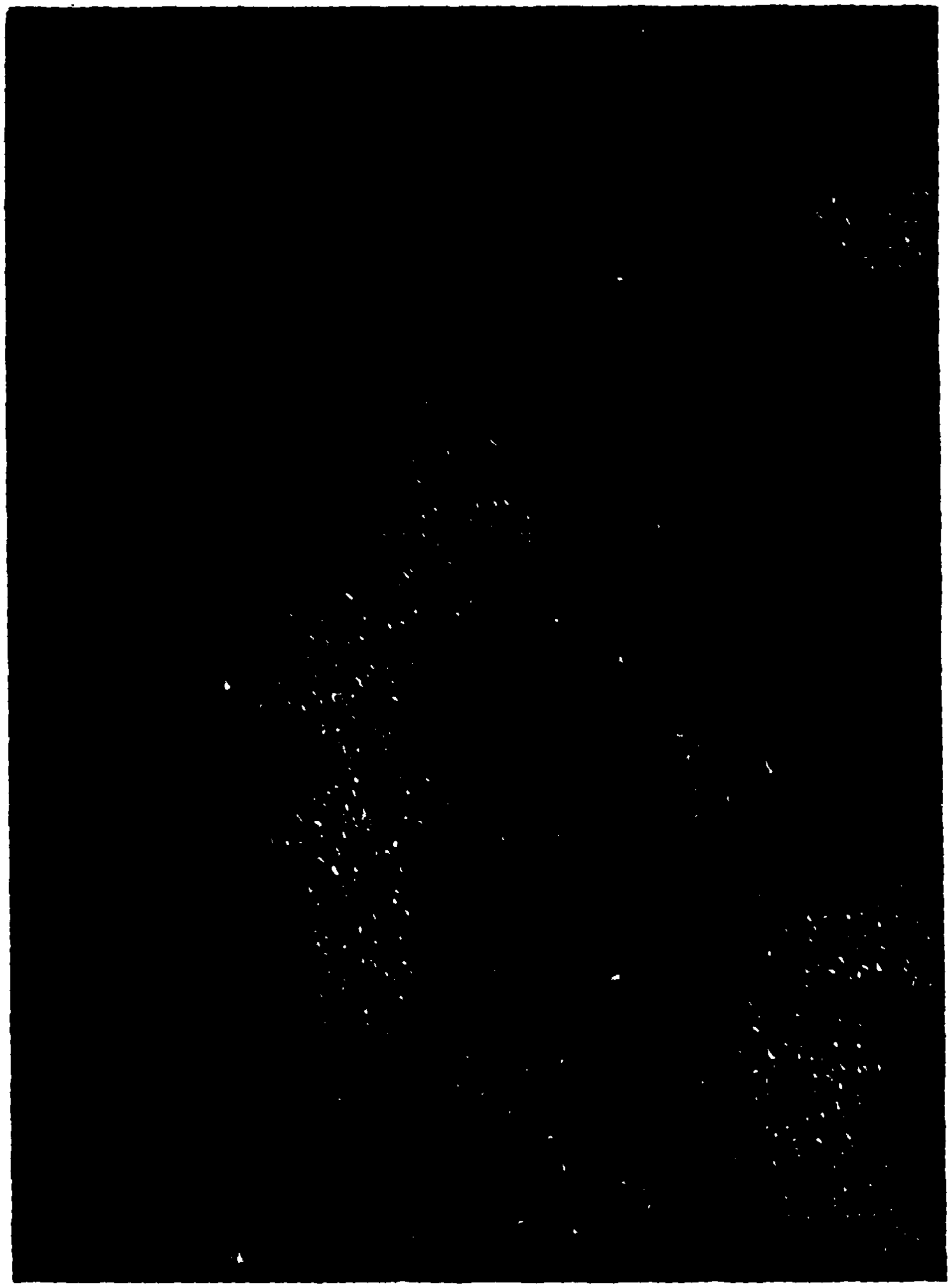


FIG 5a

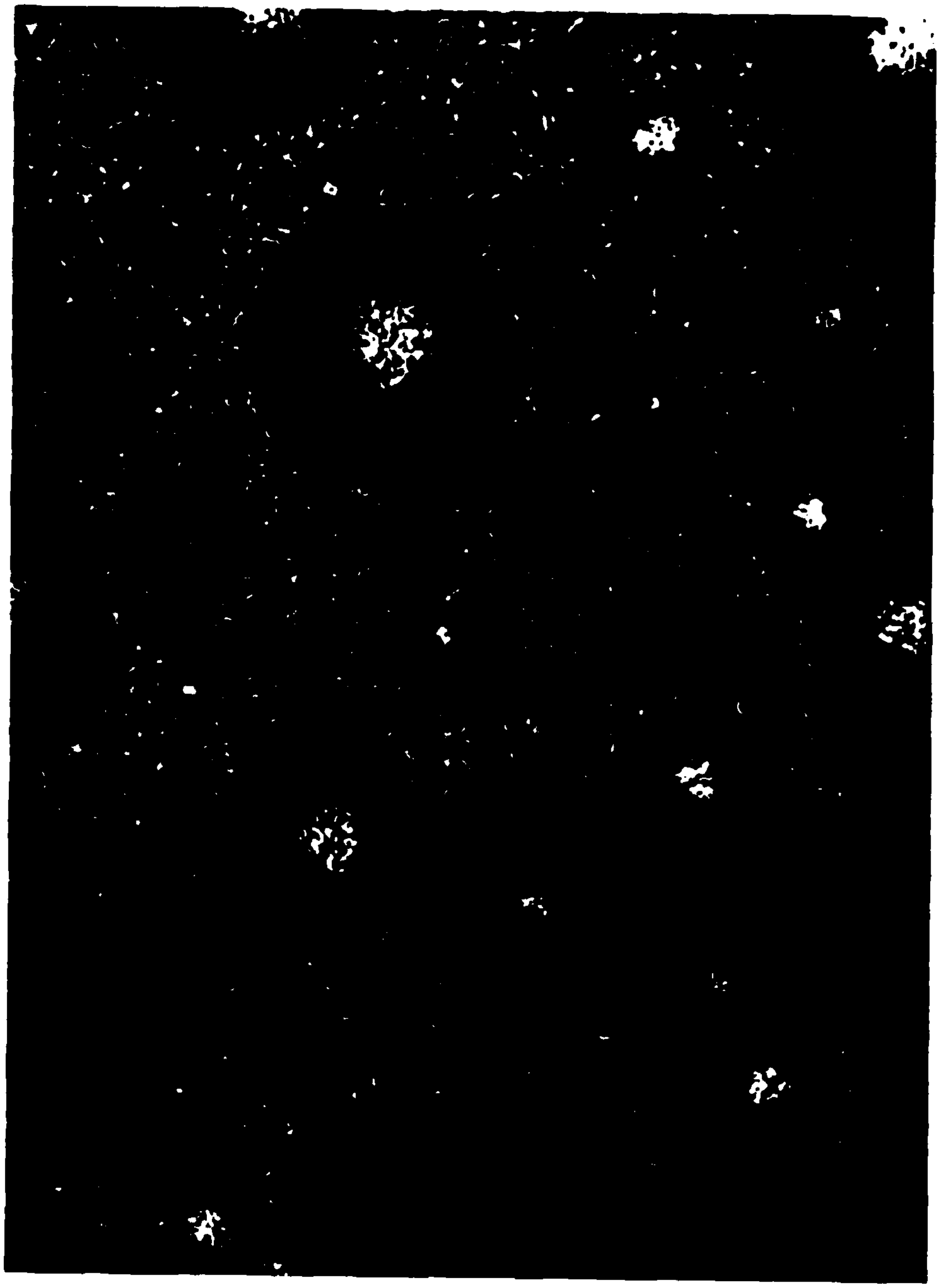


FIG 5b

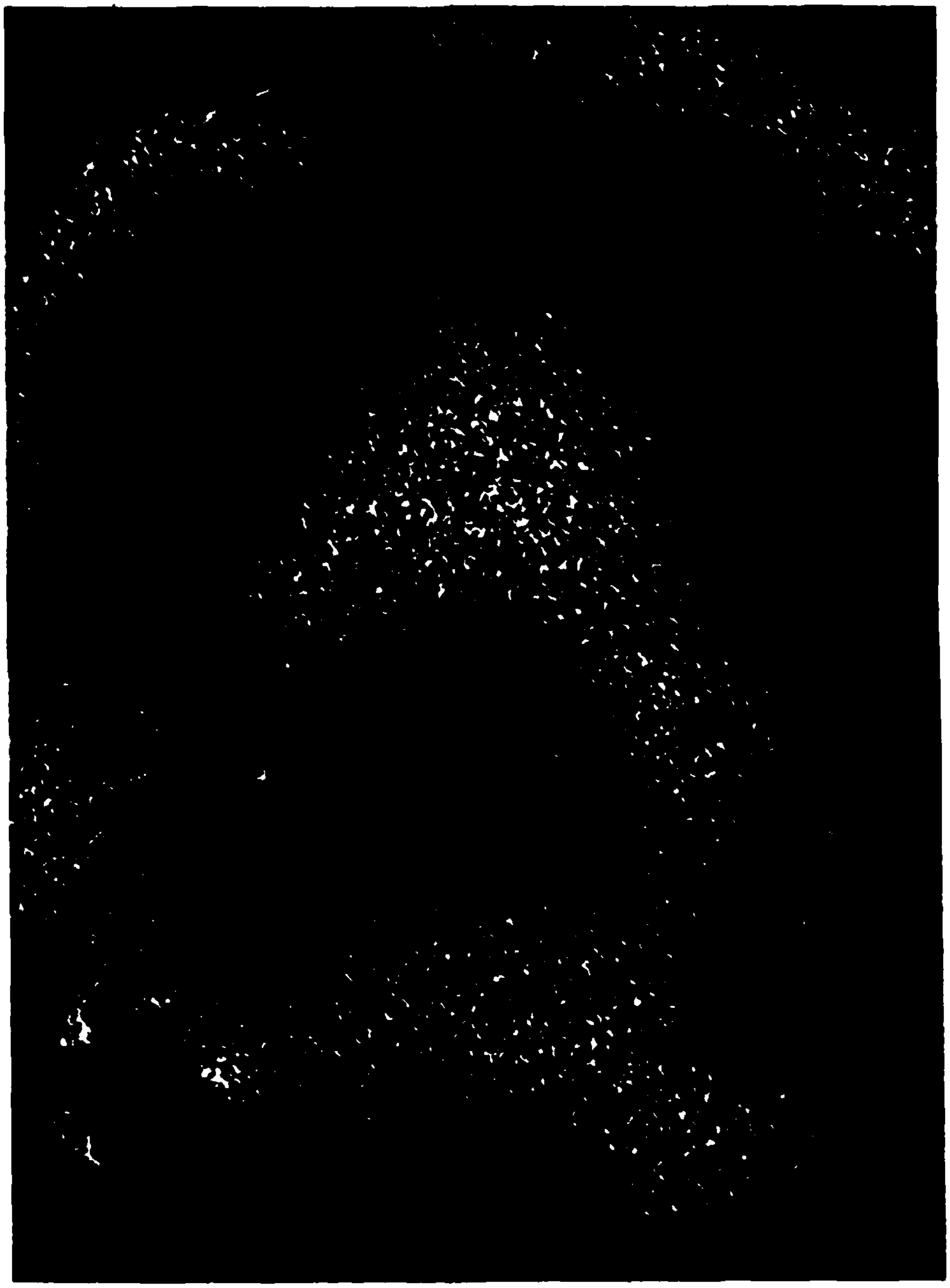


FIG 5c

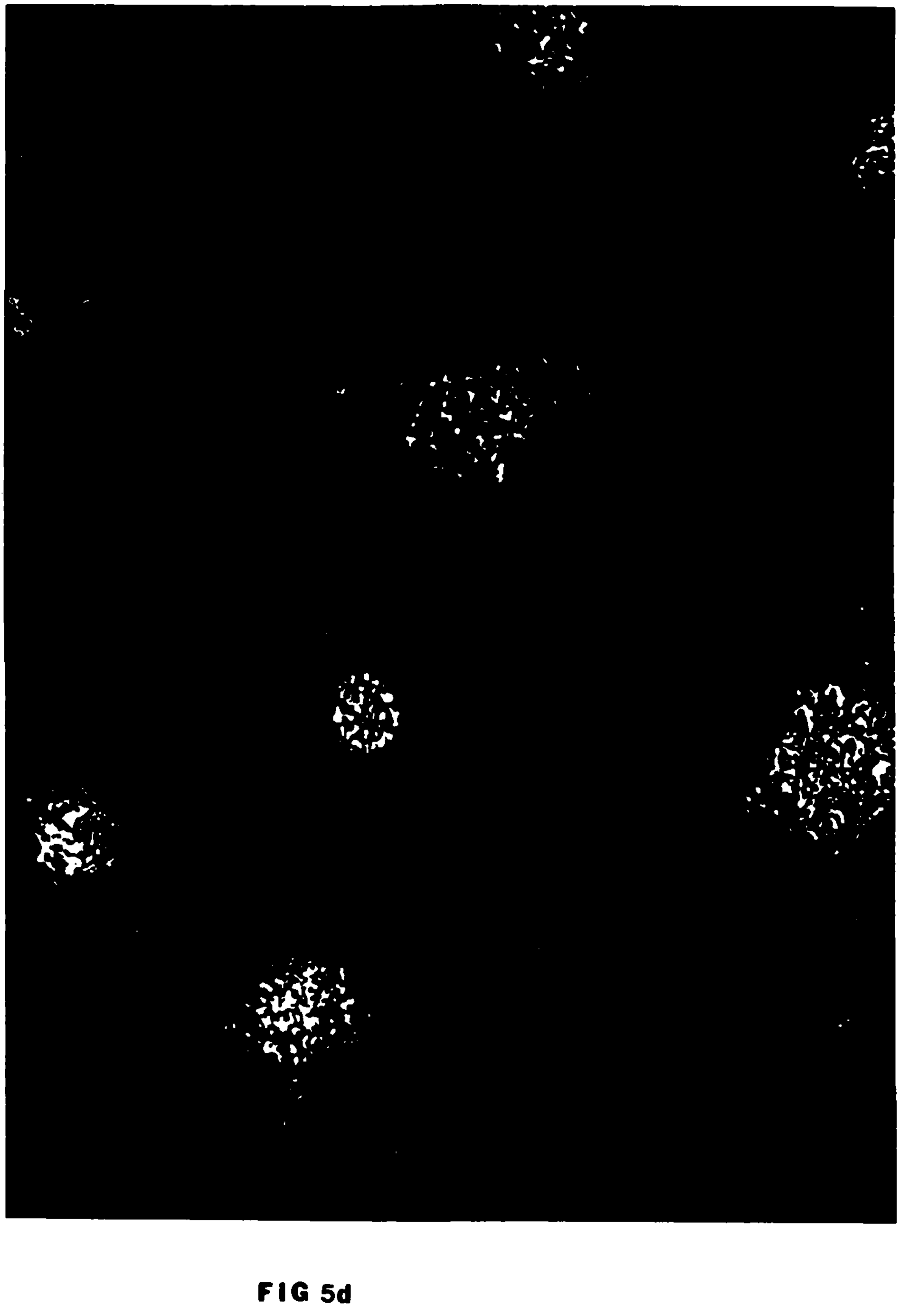


FIG 5d

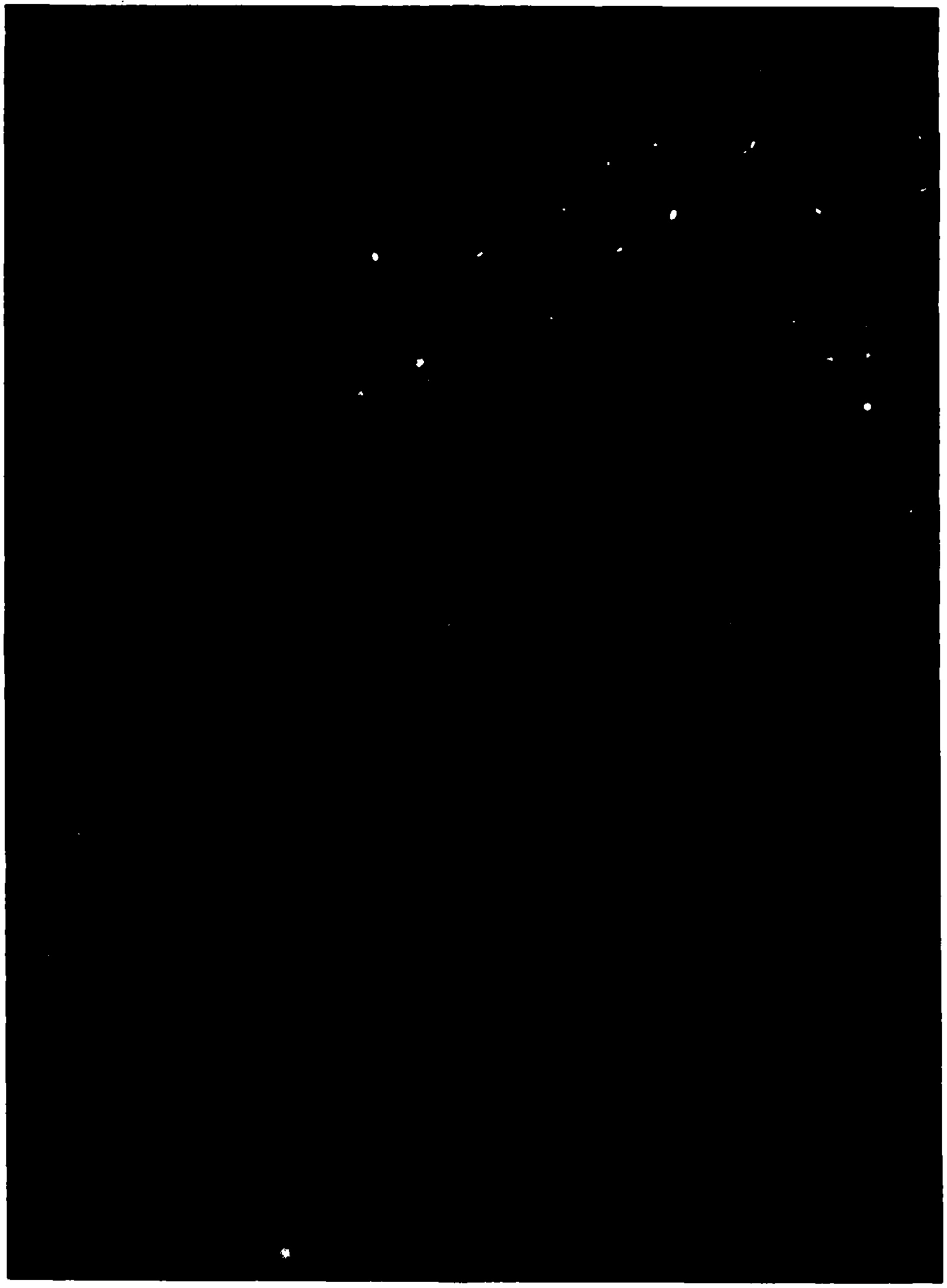


FIG 5e

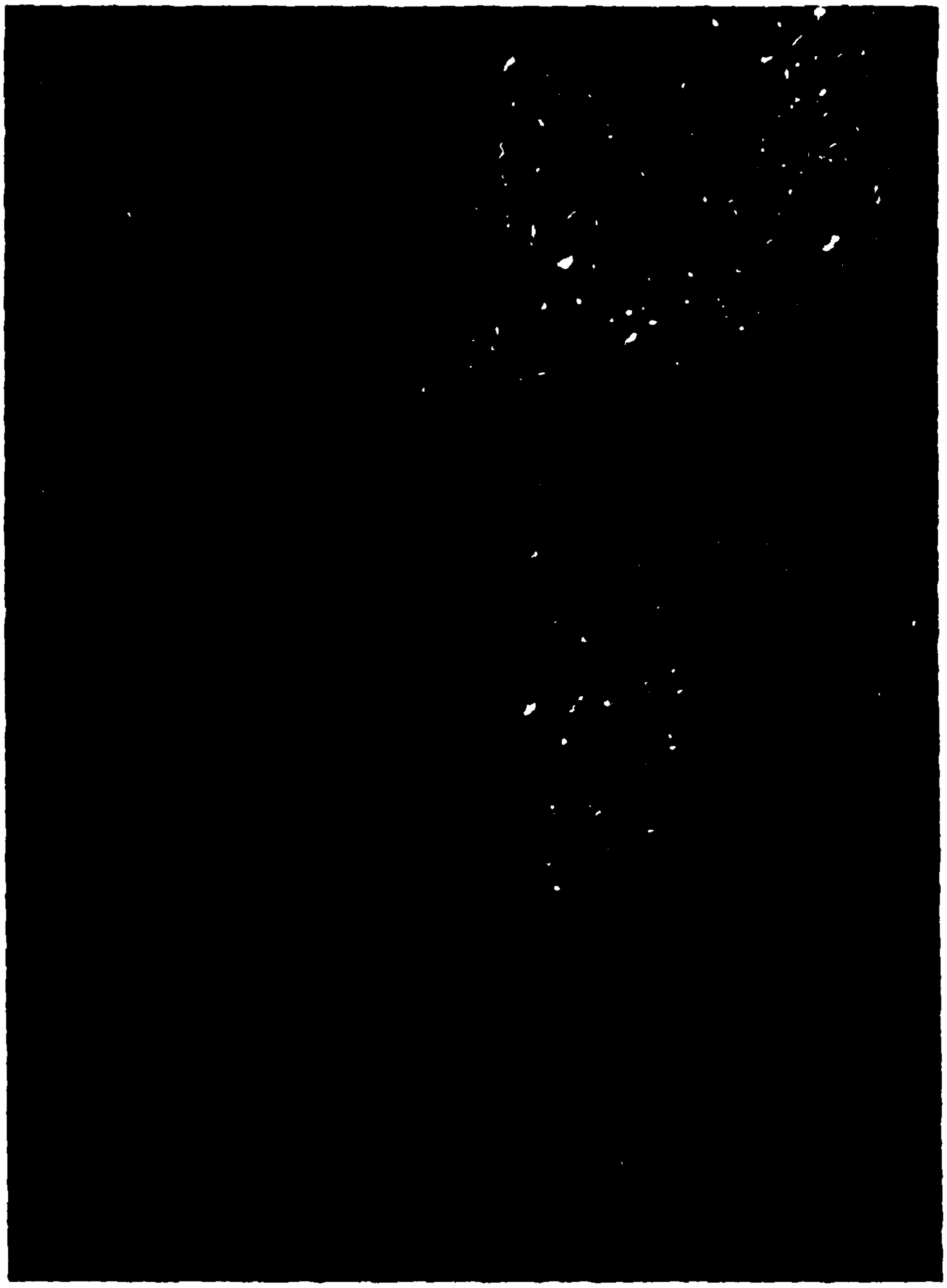
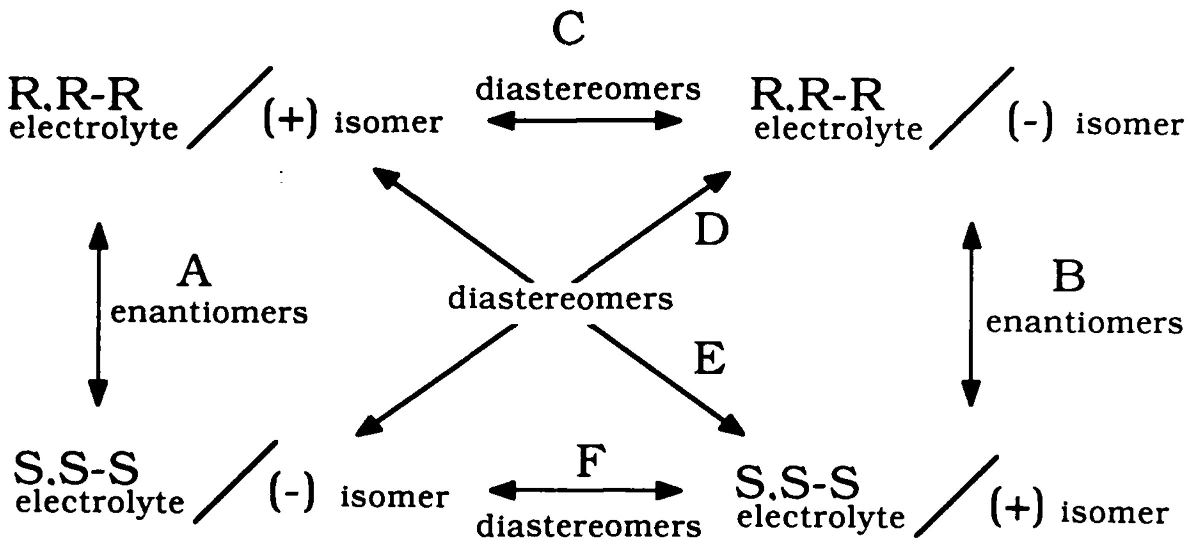


FIG 5f


R,R-R
electrolyte
(+) isomer
C
diastereomers
R,R-R
electrolyte
(-) isomer
A
enantiomers
D
diastereomers
E
B
enantiomers
S,S-S
electrolyte
(-) isomer
F
diastereomers
S,S-S
electrolyte
(+) isomer

SCHEME I

Table I Specific Rotations of Compounds Used in Preparation of Optically Active Electrolytes

Species	Observed Rotation	Reported Rotation*
R(-) 10-camphor sulfonic acid, ammonium salt	$[\alpha]_D^{20}=-19.4°$ c=4.59,H_2O	$[\alpha]_D^{20}=-18.4°$ c=5.3,H_2O
S(+) 10-camphor sulfonic acid	$[\alpha]_D^{20}=+20.9°$ c=2.00, H_2O	$[\alpha]_D^{22}=+19.9°$ c=2, H_2O
S,S(+) 2,3 dimethoxy bis 1,4 dimethyl amino butane	$[\alpha]_D^{22}=+12.78°$ neat	$[\alpha]_D^{22}=+14.5°$ neat
R,R(-) 2,3 dimethoxy bis 1,4 dimethyl amino butane	$[\alpha]_D^{22}=-12.81°$ neat	$[\alpha]_D^{23}=-14.4°$ neat
S,S(-) 2,3 dimethoxy bis 1,4 trimethyl ammonium butane diiodide	$[\alpha]_D^{20}=-40.3°$ c=2.5, H_2O	
R,R(+) 2,3 dimethoxy bis 1,4 trimethyl ammonium butane diiodide	$[\alpha]_D^{20}=+40.2°$ c=4.54, H_2O	

* Values were taken from Aldrich catalog, 1986-1987.

Table II Specific Rotations of Optically Active Electrolytes Prepared by Ion-Exchange

Species[*]	Observed Rotation	Calculated Rotation[†]
S,S-S	$[\alpha]_D^{24}=-11.7^\circ$ c=3.48, H_2O	$[\alpha]_D^{20}=-14.3^\circ$
R,R-R	$[\alpha]_D^{24}=+11.6^\circ$ c=3.48, H_2O	$[\alpha]_D^{20}=+14.3^\circ$
S,S-R	$[\alpha]_D^{24}=-39.74^\circ$ c=3.48, H_2O	$[\alpha]_D^{20}=-42.1^\circ$

[*] See Experimental section of text for abbreviations.

[†] Values were calculated from data in Table I.

Table III Slopes for Peak Current vs. Square Root of Scan Rate for Native and Modified Glassy Carbon in Aqueous Electrolytes {$\mu A(s/mV)^{1/2}$}.

Species	(+) $Ru(bpy)_3^{3+/2+}$		(-) $Ru(bpy)_3^{3+/2+}$	
Scan Direction	Anodic	Cathodic	Anodic	Cathodic
Native	1.10	1.08	1.21	1.06
($KClO_4$)	1.29	1.08	1.24	1.03
Film	0.703	0.638	0.901	0.818
($KClO_4$)			0.900	0.827
Film	0.668	0.629	0.888	0.795
(KNO_3)	0.640	0.590	0.794	0.735

Table IV Slopes for Peak Current versus Square Root of Scan Rate for Native and Modified Glassy Carbon in COC saturated Acetonitrile / TBAP $\{\mu A(s/mV)^{1/2}\}$.

Species	(+) $Ru(bpy)_3^{3+/2+}$		(-) $Ru(bpy)_3^{3+/2+}$	
Scan Direction	Anodic	Cathodic	Anodic	Cathodic
Native	1.58	1.36	1.66	1.44
	1.70	1.49	1.69	1.51
Film	1.26	1.29	1.44	1.28
	1.36	1.22	1.47	1.54

Table V Slopes for Peak Current versus Square Root of Scan Rate for Native and Modified Platinum in COC saturated Acetonitrile / TBAP ($\mu A(s/mV)^{1/2}$).

Species	(+) $Ru(bpy)_3^{3+/2+}$		(-) $Ru(bpy)_3^{3+/2+}$	
Scan Direction	Anodic	Cathodic	Anodic	Cathodic
Native	0.480	0.478	0.465	0.450
	0.466	0.491		
Film	0.445	0.413	0.460	0.426
	0.481	0.436	0.488	0.452

Table VI Slopes for Peak Current vs. Square Root of the Scan Rate for Native and Glassy Carbon in Chiral Electrolytes {$\mu A(s/mV)^{1/2}$}.

Electrolyte	Electrode Condition	Redox Couple	
		(+)Ru(bpy)$_3^{3+/2+}$	(-)Ru(bpy)$_3^{3+/2+}$
R,R-R	Native	0.669	0.624
		0.629	0.603
		0.633	0.628
			0.609
	Film	0.541	0.527
		0.553	0.536
S,S-S	Native	0.617	0.671
		0.623	0.699
	Film	0.540	0.563
		0.522	0.588
		0.495	0.543
S,S-R	Native	0.633	0.609
		0.641	0.662
			0.626
	Film	0.534	0.509
		0.512	0.523

Table VII Percent Difference* in Anodic Slopes for the Pairs of Stereoisomers In Scheme I.

Stereoisomer Pair	Nature of Stereoisomerism	Percent Difference
A	Enantiomers	2.2%
B	Enantiomers	0.6%
C	Diastereomers	4.4%
D	Diastereomers	6.6%
E	Diastereomers	3.8%
F	Diastereomers	5.9%

* Values were calculated from the averages of the anodic slopes for the <u>native</u> electrode cases in Table VI.

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