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Research is reported on the use of thermodynamically reversible dopant solubilities (and electro-solubilities), in conducting polymers, for the study of ionization mechanisms, band structure, and carrier species. Both theory and experiment is accomplished. Much work is focused on iodine in polythiophene and protons in emeraldine. Studies of conducting polymer films as gas selective membranes are performed. The results are dramatic; conducting polymers appear to be exceptionally good gas selective membranes.

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COMPLETED PROJECT SUMMARY

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PUBLICATIONS:

1. "Holes, Electrons, Polarons, and Bipolarons and the Thermodynamics of Electrically Active Dopants", H. Reiss and Dai-uk Kim, in Nonlinear Optical and Electroactive Polymers", eds. P. N. Prasad and D. R. Ulrich (Plenum Publishing Corporation, New York, 1988).

2. "Determination of Electonic Species in Electroactive Polymers", H. Reiss, J. Phys. Chem. 91, 5164 (1987).

   "Theoretical Analysis of Protonic Acid Doping of the Emeraldine Form of Polyaniline." H. Reiss, J. Phys. Chem. 92, 3657 (1988).

3. "Thermodynamically Reversible Uptake of Electrically Active Dopants in Conducting Polymers: Iodine in Polythiophene." Dai-uk Kim, H. Reiss, Journal of the Electrochemical society, 135, No. 6, 247C (1988).

5. "Numerical Analysis of Diffusion in the Presence of Nonlinear Trapping." W. D. Murphy, H. M. Rabeony, and H. Reiss. J. Phys. Chem. 92, 7007 (1988).

6. "Note on the Theory of Protonic Acid Doping of Polyaniline." H. Reiss, Synthetic Metals 30, 257 (1989).

Papers in Preparation

7. "Rectification Without Bulk Carrier Gradients." H. Reiss and D. Swanson.

8. "Modified Donnan Equilibrium in the Proton Doping of Emeraldine." E. Scherr and H. Reiss.

9. "Isobestic and Related Phenomena in the Internal Redox Behavior of Polyanilines." J. Masters and H. Reiss.

10. "Voltaic Control of the Adsorption of Iodine Vapor by Polythiophene." Dai-uk Kim and H. Reiss.

11. "Emeraldine as a Gas Selective Membrane." M. E. Anderson, R. B. Kaner, and H. Reiss.

Patent Disclosure:

"Conducting Polymer Membranes for Gas Separation", UC Case No. 89-201-1, Mark Anderson, Howard Reiss, Benjamin Mattes, and R. B., Kaner.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objectives of this research were centered on the application of physical chemical (thermodynamic) techniques to the study, in conducting polymers, of 1) mechanisms of ionization of electroactive dopants, 2) band structure, and 3) carrier species, by measuring the thermodynamically reversible, equilibrium solubilities (and electrosolubilities) of dopants in polymers. As part of this program, phenomena were to be investigated for technological application when opportunities presented themselves.

Accomplishments reflect a response to these objectives:

It was proved (in spite of existing doubt) that dopant-polymer systems exist, e. g., iodine (vapor) -polythiophene, for which thermodynamically reversible solubility is attainable. Absence of hysteresis in the absorption–desorption isotherm (measured with a quartz microbalance) was demonstrated. Furthermore, the existence of steplike concentration profiles for diffusing dopants in conducting polymers as well as the great disparity between times for diffusion in and out were proved, on the basis of theory, to be entirely compatible with thermodynamic reversibility.

The dramatic, temperature independent discontinuity in isotherm slope at saturation , for iodine absorbed in polythiophene films on gold, as opposed to polythiophene powder, was reaffirmed. Furthermore, it was shown (still using the quartz microbalance) that involvement of the gold layer as the negative plate of a capacitance (not bridging the film) eliminated the discontinuity in isotherm slope, thereby demonstrating that the sharp discontinuity was somehow connected to the Schottky junction formed by the film and the layer of gold.

Simultaneous measurements of conductivity (fc.. ⁻ .nt probe) and reversible absorption provided evidence (using the proposed method) for the formation of bipolarons in the case of iodine in polythiophene.

In another direction a theory was developed to allow the determination of carrier species, e.g., polarons or bipolarons, through the measurement of the thermodynamically reversible potential of a doped conducting polymer serving as an electode in contact with a solution containing the dopant. In the same context a careful critical review of the concept of the absolute electrode potential was undertaken and eventually published as a "feature article" in the Journal of the Electrochemical Society.

In yet another direction, but still in an effort to demonstrate thermodynamically reversible uptake of dopant, a statistical mechanical (equilibrium) theory for the proton doping of emeraldine as a function of pH was developed and applied to the measurements of MacDiarmid et al. The theory suggested that the original curves, drawn through the data as a "best fit". were not compatible with theory. A compatible curve was drawn, and additional measurements by MacDiarmid's group confirmed the new curve.

In another study, directed at the technological application of conducting polymers, the usefulness of conducting polymers as gas selective membranes was investigated. Emeraldine (polyaniline), suitably prepared, was found (among other things) to be an excellent separator of both helium and oxygen from nitrogen. The separation ratios He/N_2 and O_2/N_2 were found, respectively, to be 3500 and 50 to 1.0. These Figures are the best, published in the open literature, for any membrane. The reasons for these high separation ratios are still being studied. At least in the case of O_2/N_2 they appear to be connected to the "conductive" polymer nature of the membrane.

In a related study, not yet complete, an "active" as opposed to a "passive" membrane has been fabricated by depositing a thin layer (~ 10 nm) of metal on the conducting polymer film so as to form a Schottky junction. Application of a small (~ 1.0 volt) reverse bias to this junction should enable one to "tune" to the separation of one or another gas.

A collaborative effort on conducting polymer gas selective membranes has now been initiated with A. G. MacDiarmid's group at the University of Pennsylvania.

With partial support from the present contract, the principal investigator (H. Reiss) was able to spend three months (April, May, June 1989) in MacDiarmid's laboratory. Several collaborative research projects with MacDiarmid's students were initiated and are now complete enough for publication.

One project deals with the possibility of rectification even when "bulk" doping levels in conducting polymers are uniform on the course-grained macroscopic level. Microscopic conditions under which such rectification is possible are elucidated.

Another project concerns, the "Donnan equilibrium" in the case of an ion exchange membrane in which the "fixed ions" are only partly fixed, i. e., in the case where they are partly

dissociable as in the case of protons bound (adsorbed) to emeraldine. Theory and experiment has been completed with substantial mutual agreement. The results are important for assessing the absence of hysteresis in the emeraldine-proton absorption curves.

A final project involves the exploration of the remarkable isobestic behavior of mixtures of leucoemeraldine and pernigraniline dissolved in NMP. The isobestic points reflect redox reaction and equilibrium between the two dissoved polymers. Theory and experiment seem to agree.

Chemical-Like Behavior of
Electrons and Holes in
Polymeric Conductors

I. **Introduction**

The objectives of this project, as stated in the original proposal, were centered on the application of physical chemical techniques to the study, in conducting polymers of 1) mechanisms of ionization, of electrically active dopants, 2) band structure, and 3) carrier species. In this context "physical chemical techniques" meant the study of the equilibrium distribution (solubility) of an electrically active dopant between an external phase and the conducting polymer. In even simpler terms, it meant the application of the law of mass action and the measurement of associated equilibrium constants in order to elucidate the relevant mechanisms.

An extremely simple example of such an approach, not involving a conducting polymer, can be found in the dissolving of hydrogen gas in palladium. Here, the solubility is proportional to the square root of the hydrogen pressure, and the law of mass action tells us that this dependence implies the dissociation of dissolved H_2 so that hydrogen in palladium must be atomic rather than molecular. Thus one learns something about the state of the solute from such equilibrium studies.

Similar approaches (1,2) have been taken in the study of dopants in ordinary (crystalline) semiconductors. There, not only was it possible to obtain information on carrier species and ionization mechanisms, but on band structure as well. This was accomplished by measuring the relevant equilibrium constants as functions of temperature. The corresponding "heats of reaction", determinable in this way, often corresponded to electronic transitions between band levels.

Such an approach, when it is feasible, offers several advantages. For example, being a thermodynamically reversible equilibrium measurement it is not subject to many of the uncertainties that beset an irreversible measurement, i.e., a transport measurement such as resistivity. In the case of resistivity, for example, the dominant process could (in conducting polymers) be the interchain hopping of electrons, so that the intrinsic carrier mobilities within a single polymer molecule could be masked. In contrast, the reversible measurement furnishes

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more direct information on just these intrinsic intramolecular properites. Furthermore, in principle, the reversible measurement can "stand alone" and yield information without requirng additional information of a molecular nature. For example, to fully exploit the information provided by a measurement of infrared reflectance (3), it is necessary to know the plasma frequency, and this in turn requires knowledge of the electron or hole effective mass.

When the work proposed under the subject contract was initiated many workers in the conducting polymer field voiced considerable doubt that thermodynamically reversible solubility measurements were in fact possible with conducting polymers. Among the arguments advanced to support this view were 1) the high levels of doping, 2) "staging", conformational changes, etc., 3) hysteresis in the doping process -- large disparities in the times required for doping and dedoping, and 4) permanent chemical changes. It was widely thought that chemical reversibility (ultimate removability of all dopant) was possible, but not thermodynamic reversibility. As a result one of the important goals of our research became the discovery and demonstration of dopant-polymer systems in which true thermodynamic reversibility was possible.

As the research progressed, however, additional objectives were formulated in order to exploit newly discovered phenomena. These involved 1) the development of electrochemical theory to be used in conjunction with a thermodynamically reversible conducting polymer electrode for the determination of carrier species (e.g., bipolarons) and a concomitant analysis of the concept of the absolute electrode potential, 2) the study of various phenomena associated with the proton doping of polyaniline, including a statistical mechanical theory of cooperativity in emeraldine, 3) an analysis of a modified Donnan equilibrium (theory and experiment), 4) a study (theory and experiment) of isobestic points in the spectra of solutions of leucoemeraldine and pernigraniline in NMP, 5) a theory explaining the occurrence of rectification in uniformly doped conducting polymer, and 6) research into the gas selective membrane qualities of conducting polymers (emeraldine).

Items 3, 4, and 5 were performed in collaboration with the laboratory of A. G. MacDiarmid at the University of Pennsylvania where the principal investigator (H. Reiss) spent three months (April, May and June of 1989) with the partial support of the contract.

Item 6 proved to be very exciting. Emeraldine films, properly treated, emerged as outstanding separators of helium, hydrogen, and oxygen from nitrogen. Indeed the separation ratios (without optimization) He/N_2 and O_2/N_2 were respectively 3500/1 and 50/1. These

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exceeded the best values found in the open literatre (4) for any preexisting film. The separation of hydrogen from nitrogen in petroleum cracking plants is currently performed by gas selective membranes and represents an annual business of 750 million dollars, nationally (5). UCLA is in the process of making a patent disclosure concerning conductive polymer films as gas selective membranes. Our group at UCLA has constructed a membrane permeation apparatus for the Pennsylvania group under A. G. MacDiarmid and a collaborative effort in gas separation is underway. The Pennsylvania group has outstanding preparative capabiliues and the joint effort should be very profitable.

A goal that we are pursuing at UCLA in connection with conducting polymer gas selective membranes is the fabrication of an "active" as opposed to a "passive" membrane. With the active membrane it may be possible to "tune" to the separation of a particular gas with the application of a small external voltage bias (~ 1.0 volt).

A total of eleven papers, reporting the work of this contract, will be published. Six of them are already in print. The remaining five are in preparation and preprints (not yet in final form) of most of them are available. Both reprints and preprints are being submitted along with this report. There is also the above mentioned patent disclosure. A list of these papers and the patent disclosure appears as section II. In section III we elaborate further on the accomplishments mentioned in the present section.

II.   Publications and Patent Disclosure.

Publications:

1.   "Holes, Electrons, Polarons, and Bipolarons and the Thermodynamics of Electrically Active Dopants", H. Reiss and Dai-uk Kim, in Nonlinear Optical and Electroactive Polymers", eds. P. N. Prasad and D. R. Ulrich (Plenum Publishing Corporation, New York, 1988).

2.   "Determination of Electonic Species in Electroactive Polymers", H. Reiss, J. Phys. Chem. 91, 5164 (1987).

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     .ymers: Iodine in Polythiophene." Dai-uk Kim, H. Reiss, Journal of the Electrochemical
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Anderson, Howard Reiss, Benjamin Mattes, and R. B., Kaner.

III. **Research Accomplishments.**

In this section we provide a more thorough description of the research referred to in section I.
However, since much of it has already been described in both interim and annual reports, and
is also available in the papers accompanying this final report, the present description,
although more detailed than that of section I, will not be exhaustive:

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A. Adsorption of Iodine by Polythiophene.

An initial study (6) of the absorption of iodine vapor by polythiophene films and powders had been made, prior to the contract initiation date. Absorption isotherms were measured by the determination of film weight using a quartz microbalance within a glass housing where the iodine pressure and temperature could be controlled. Iodine pressure was measured by means of optical absorption.

The polythiophene films were initially about 200 nm thick and deposited on gold substrates of thickness 7.5 nm. The gold, in turn, was deposited on a glass coverslip. Polythiophene powder was free standing. Figure 1 exhibits some of the data as micromoles of I_2 absorbed versus iodine pressure in torr. Open circles refer to film and filled circles to powder. In each case the weights of film and powder were identical.

The film exhibits a remarkable discontinuous break to saturation at a pressure of about 0.68 Torr, independent of temperature. The powder shows no such break. The origin of the break is not yet understood but is thought to be connected with the Schottky junction that presumably exists at the interface between the film and the gold. The introduction of helium gas in addition to iodine vapor moves the break to lower iodine pressure.

Work on these absorption isotherms was continued with support of the contract. A four point probe was used to measure film conductivity as a function of iodine pressure. Results are shown in Figure 2 where the logarithm of conductivity σ is plotted against the logarithm of iodine pressure. Again, the discontinuous breaks to saturation appear. The break is, moreover, to lower iodine pressure in the presence of helium. the slope of the curve in Figure 2 is $2.6 \approx \frac{5}{2}$. The $\frac{5}{2}$ is explained on the basis of the stoichiometric coefficients in the thermodynamically reversible reaction

$$5I_2 \text{ (gas)} + PT_{site} \rightleftharpoons I_5^- + I_5^- \bullet (e^+)_2 \tag{1}$$
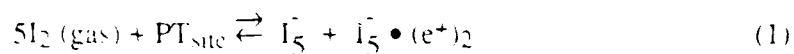
where PT indicates polythiophene and where $(e^+)_2$ represents a bipolaron. This result is the first example of the determination of carrier species by applying the law of mass action

FIGURE 1

UPTAKE OF I_2 BY POLYTHIOPHENE IN BOTH FILMS AND POWDER
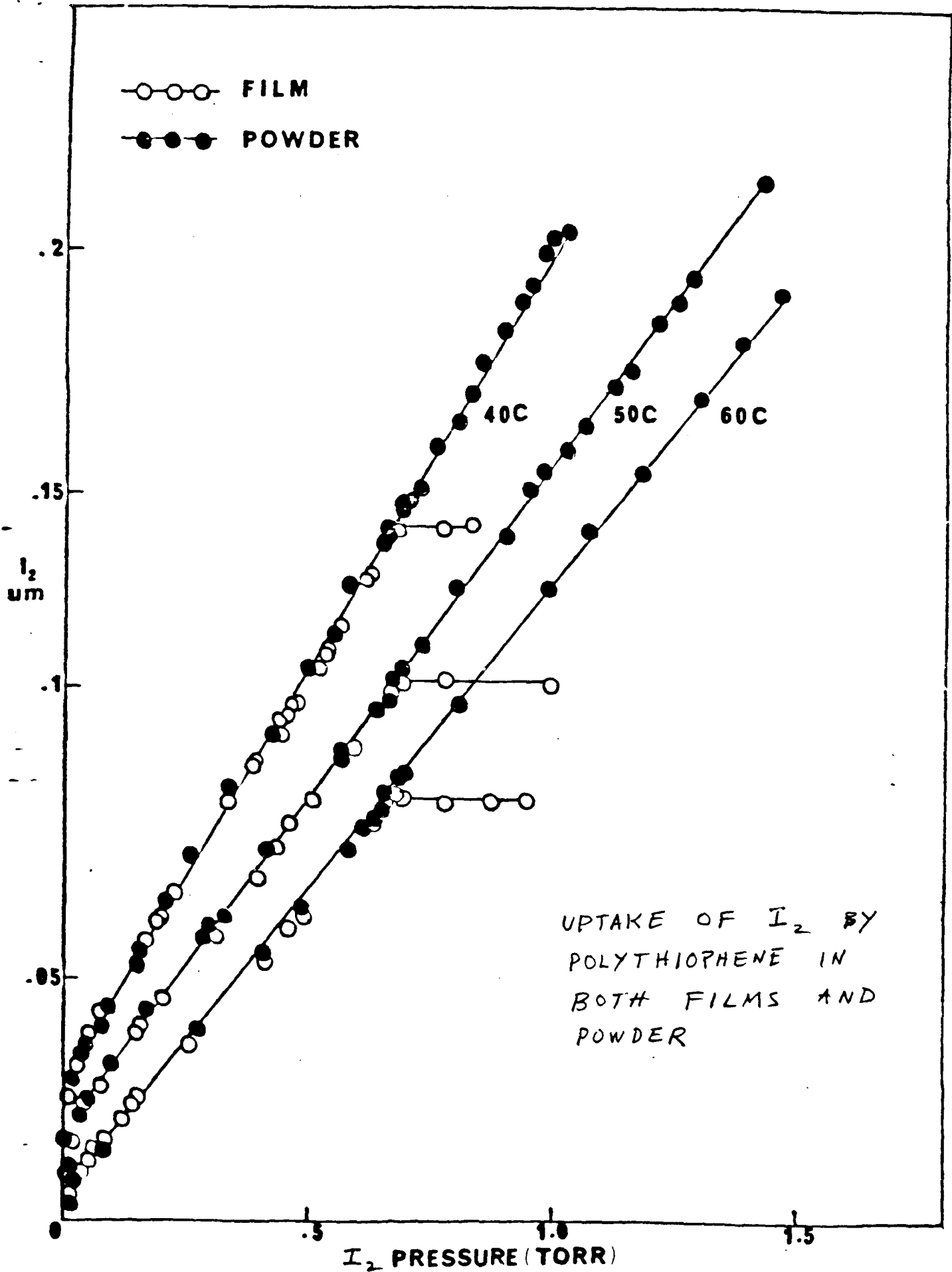
Log conductivity J versus log I_2 pressure. Discontinuous breaks to saturation still show. *SLOPE = 2.6 ≈ 5/2*
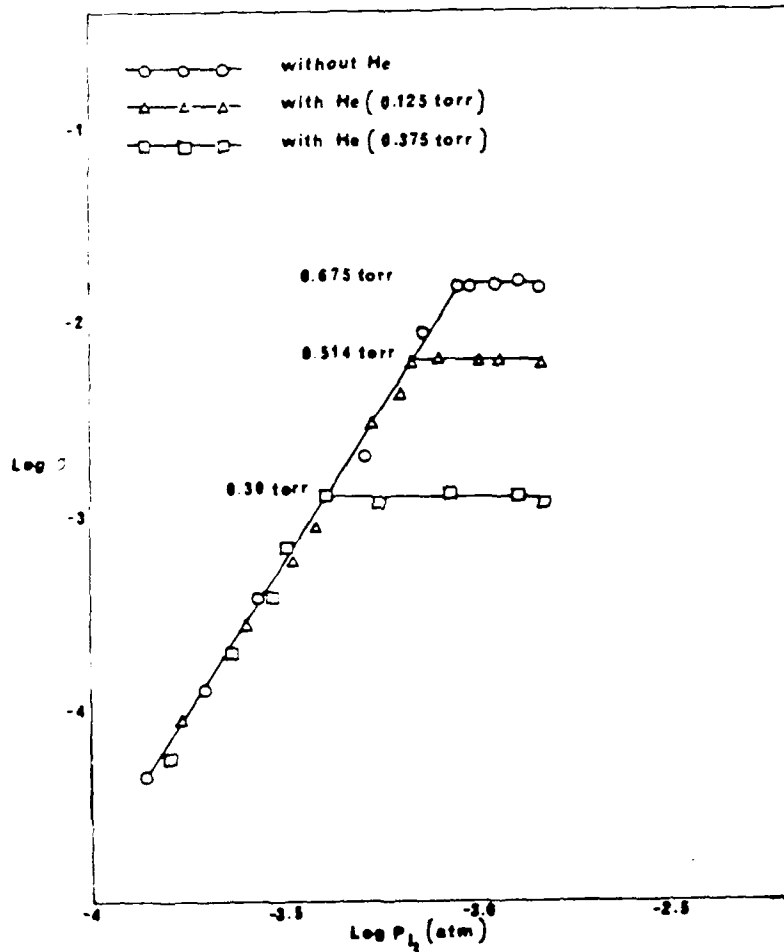

FIGURE 2

(assuming thermodynamically reversible equilibrium) to the solubility of an electrically active dopant, I_2, in a conducting polymer. As such, it addresses the earliest objectives of the proposed work.

In order to acquire further insight in to the underlying mechanism of the discontinuity in the adsorption isotherm, the structure illustrated in Figure 3 was hung from the balance and the absorption isotherm was determined in the usual manner. Again PT indicates the polythiophene film. The underlying layer of gold (Au) is shown, separated from another layer of gold by a thin layer of glass. Electrical contacts were made to both layers of gold and the potential V, as shown, was applied to the resulting capacitance-like structure. The absorption isotherm was actually measured (the film was weighed) in the presence of the applied voltage. It is important to note that the applied potential did not bridge the polythiophene film!

In spite of this, the resulting iostherms were those exhibited in Figure 4. In this case the film was about 450 nm in thickness. The solid dots, open circles, open squares, open triangles, and open diamonds are measurements in the absence of any potential, i.e.. they represent the normal absorption isotherms. The remaining symbols are points measured in the presence of the potential (negative on the gold layer attached to the film) indicated by the legend below the curve and to the right.

Once again the discontinuous break to saturation is observed in the absence of applied potential. However, as the potential is increased (negatively on the side of the film), the discontinuity gradually disappears until at - 1.0 volt it is entirely gone. Since the potential does not bridge the film the following explanation is suggested.

At the interface between the film and the substrate gold layer, there is a Schottky junction whose natural potential (determined by the work function difference between the polymer and gold phases) produces a negatively charged layer (holes, polarons) in the polymer. The action of this charged layer is what restricts the solubility of I_2 and causes saturation, since fewer electrons are available to produce I_3^-, I_5^-. Applying a negative potential (as in Figure 4) to the layer of gold resupplies electrons and once more increases the solubility, lifting the saturation. Further investigation is required before this argument can be validated.

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FIGURE 3
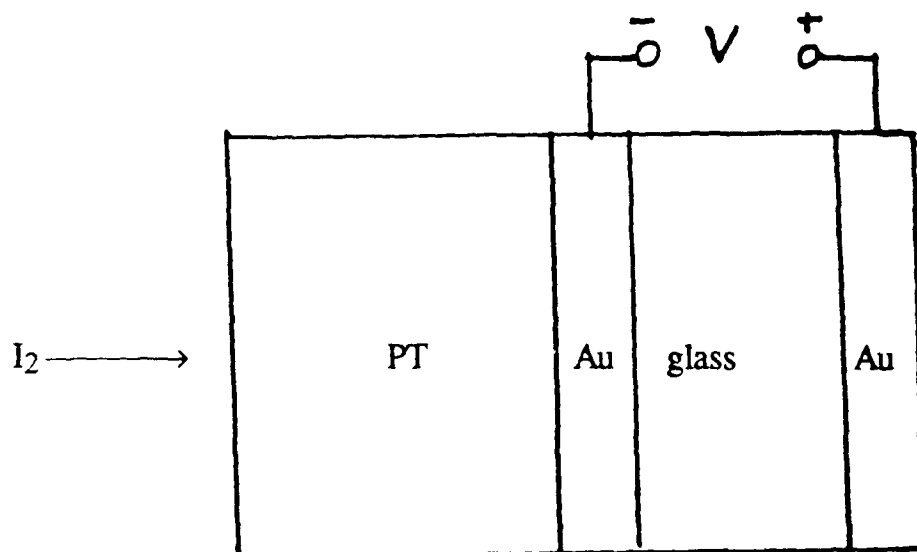
CONFIGURATION EMPLOYED IN THE
MEASUREMENT OF I_2 ABSORPTION IN
POLYTHIOPHENE WITH POTENTIAL APPLIED AS SHOWN.
Although the potential V does not bridge the polythiophene
(PT) film it removes the discontinuous break to saturation
when it reaches ~1.0 volt.

FIGURE 4
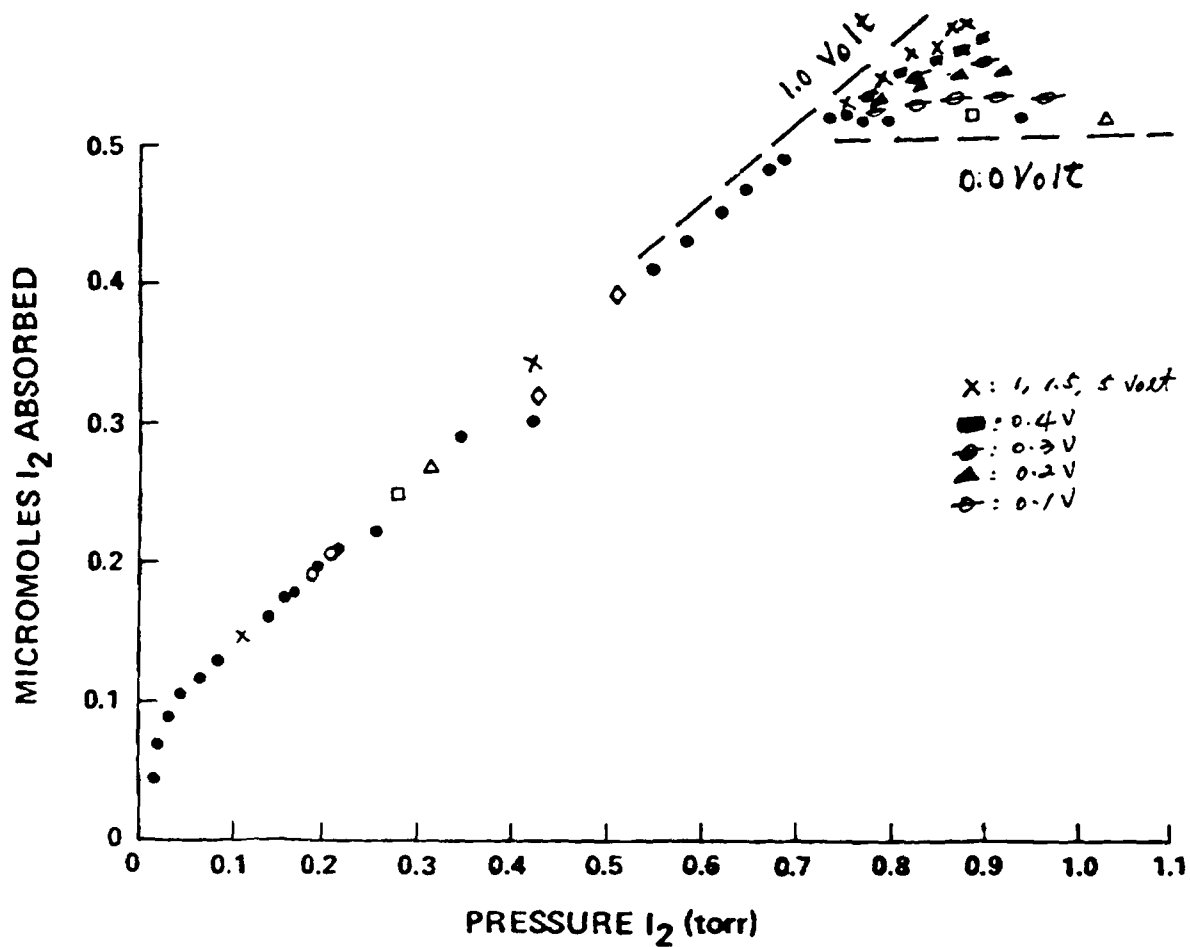
Removal of discontinuous break to saturation , by application of a 1.0 volt external potential, not bridging the conducting polymer. X's INDICATE RESULTS WITH APPLIED POTENTIAL OF 1.0 VOLT.

If the potential had bridged the polymer film, changes of doping level generated by an applied potential would have been less significant, since then an ordinary case of electrochemical doping would have been involved.

B.   Achievement of Thermodynamically Reversible Equilibrium

As indicated in section I, an important objective that developed during the course of the present contract was the demonstration that dopant-polymer systems existed in which thermodynamically reversible solubility could be obtained. The first system to be examined in this context involved iodine vapor and polythiophene film. The early work on this system, described in reference 6 did not directly address this subject. Nevertheless, here we reproduce as Figure 5, Figure 1 of reference 6.

The figure exhibits five isotherms corresponding to the temperatures 40, 50, 60, 70, and 80 C. The isotherm at 40 C is of primary importance in the study of reversibility. The open circles represent "equilibrium" uptakes of I_2 obtained by means of absorption, i.e. starting with the empty film and allowing the uptake to achieve its "equilibrium" value. The times for the various uptakes ranged from 20 to 30 minutes.

It was discovered that iodine could be completely removed from the film by placing it in vacuum; the time required for desorption exceeded that for absorption. Thus, the system was at least chemically reversible. The experiment (absorption followed by desorption) was repeated, in sequence, to produce the remaining isotherms in the figure at 50, 60, 70, and 80 C. After the same film had been carried through these additional measurements at the other temperatures, the determination of the isotherm at 40 C, using it, was repeated. The squares on the 40 C isotherm mark the results of this second determination. As it can be seen, the earlier isotherm was faithfully reproduced, including the remarkable "discontinuity to saturation" in the neighborhood of 0.68 torr. Scanning electron micrographs of the film, before and after a cycle of absorption and desorption, exhibited no obvious differences in the appearance of the film.

The fact that the same isotherm could be reproduced so faithfully, after so many cycles of absorption and desorption at several different temperatures, could hardly be explained on the basis of chemical reversibility alone. If everything (conformation, phase structure, etc.) had not been reversed, it would require a miracle of sorts to explain this reproducibility.

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UPTAKE OF I_2 BY POLYTHIOPHENE FILM ON GOLD SUBSTRATE AT VARIOUS TEMPERATURES. SQUARES REPRESENT SECOND MEASUREMENT AT 40C AFTER THE OTHER MEASUREMENTS HAD BEEN PERFORMED ON THE FILM.

40C
30C
60C
70C
80C

I_2 PRESSURE (TORR)

I_2 um
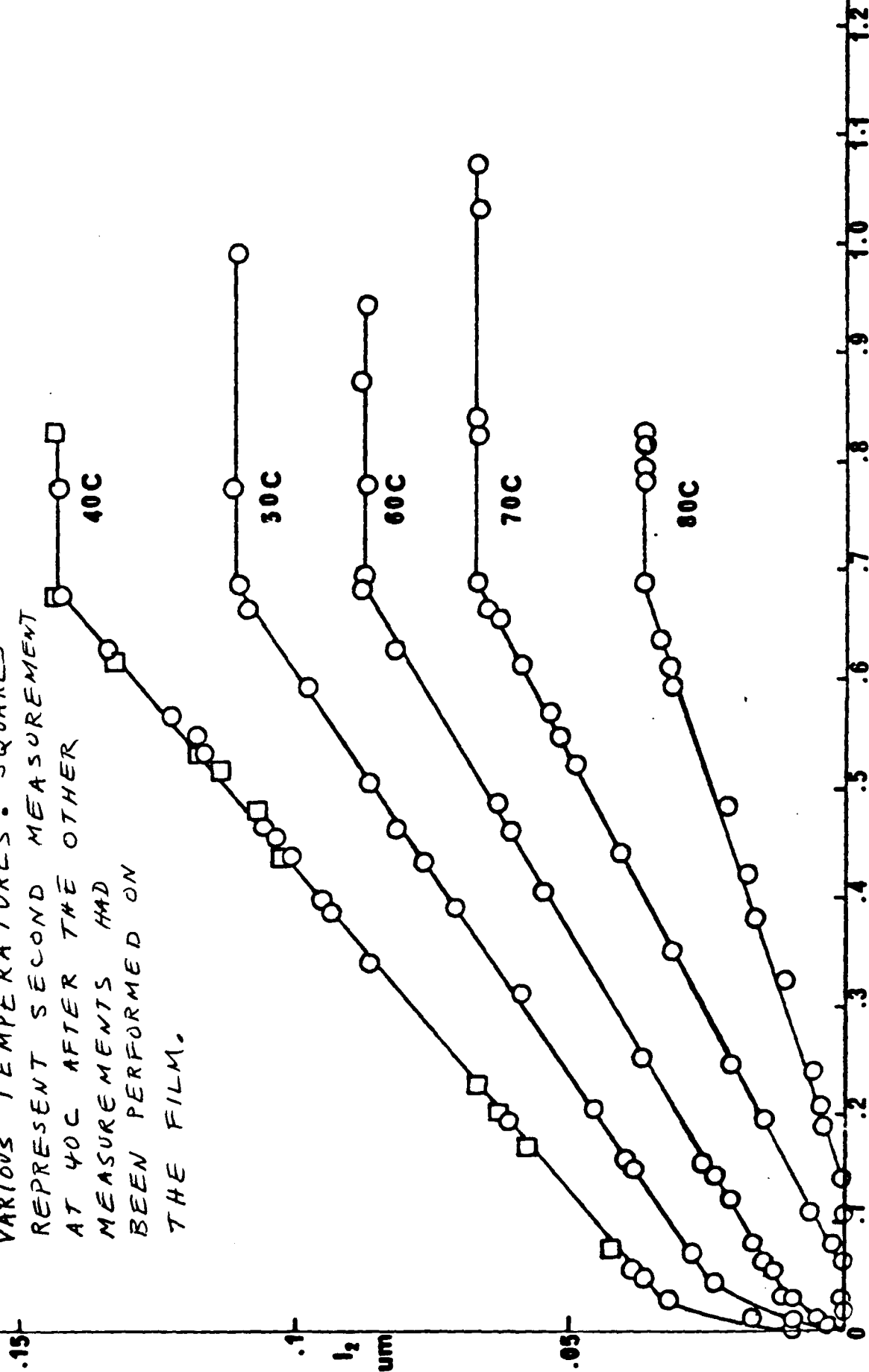
FIGURE 5

In reference 6, the issue was left at this point, and the authors proceeded to address other questions. The one experiment, also possibly crucial, not performed, was the determination of the isotherm by desorption, in an effort to reveal hysteresis.

When it became apparent that some workers still doubted the thermodynamic reversibility of the isotherms in reference 6, the additional measurements were undertaken (7). These included the desorption measurements omitted in the studies of reference 6, as well as additional absorption measurements, and were performed in the same microbalance apparatus, but on a different film. This film (87 µg of polythiophene) was about four times as thick as the one used in the earlier experiments. Consequently, considerably more time was required for both absorption and desorption, but the larger uptake increased the accuracy of the measurement. The isotherm, determined at 50 C, is exhibited in Figure 6. The filled circles represent points determined by absorption, i.e. in the manner of the isotherms of reference 6. The isotherm is plotted as micromoles of absorbed I_2 vs. I_2 pressure (torr), and the available precision of measurement was 0.0013 µmoles. This amounts to about 1/500 of the full range of the ordinate in Figure 6, and, relative to the experiment, the precision was therefore high.

The new absorption isotherm exhibited all the features of those appearing in Figure 5, including the "discontinuity to saturation" which now occurred at about 0.74 torr rather than at the 0.68 torr.

Four desorption experiments were performed, and each of these is represented, in Figure 6, by a pair of points denoted by either open circles, squares, triangles, or diamonds. Table I lists some of the data relevant to these experiments. The first two columns in the table are self evident. The third represents the total uptake of I_2 (in µg) at the points where desorption was initiated. In each experiment the film, devoid of iodine, was suspended from the balance in iodine vapor having the pressure listed in the fifth column. The uptake of I_2 to "equilibrium" at the listed pressure appears (in µg) in the third column, and the time required to achieve this equilibrium appears in the fourth column. Equilibrium was defined by the level of absorption beyond which no observable change in the weight of the film occurred during a period extending over many hours. After the attainment of absorption equilibrium. in this manner, the iodine pressure was reduced to the value appearing in column eight. and the ensuing desorption was followed by observing the loss of weight of the film. After the time. listed in column seven of the table, equilibrium was again established. Again.   .
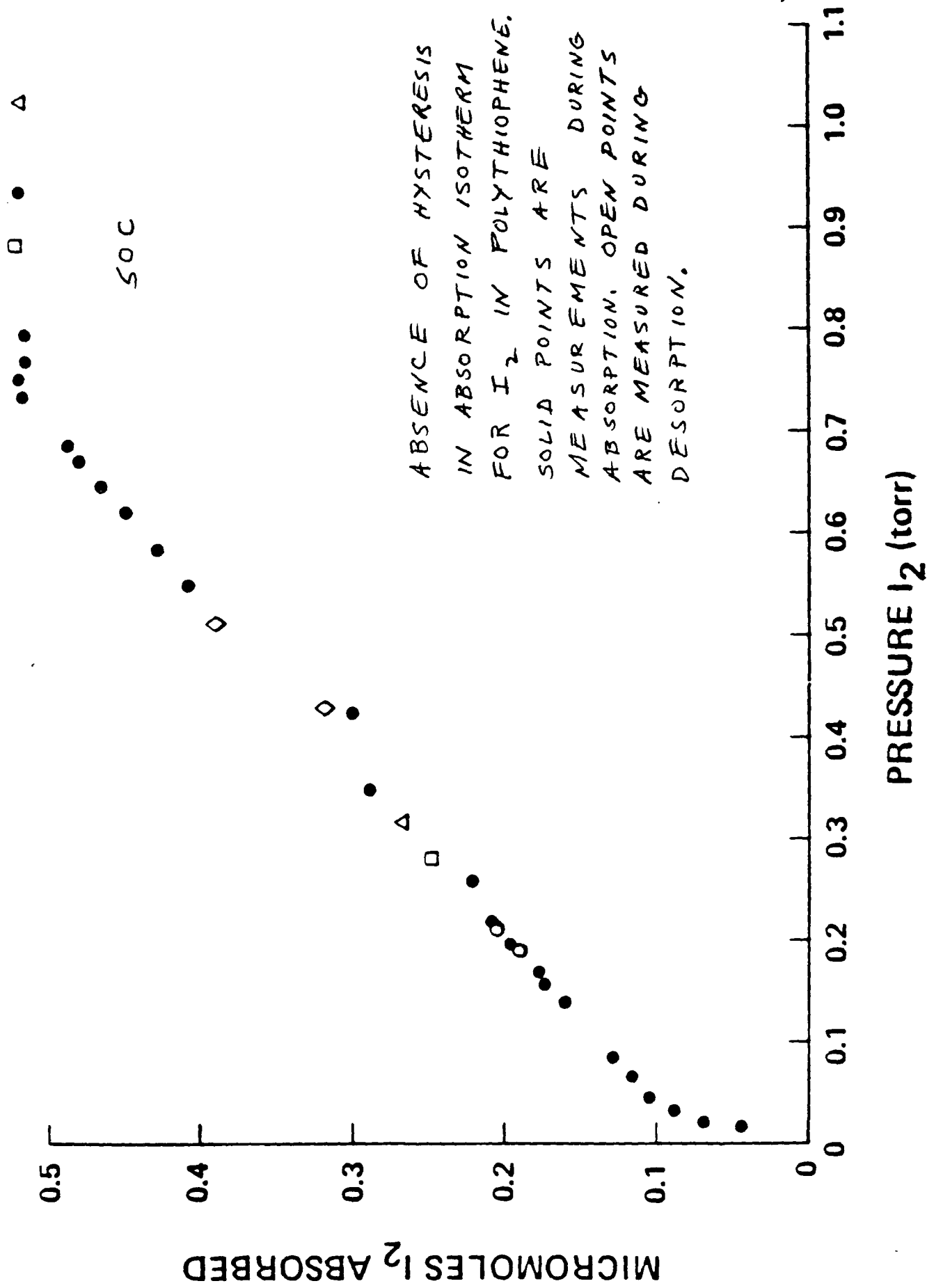
8

Table 1

Temperature = 50 C

Mass of film = 87 µg

experiment	I_2 data symbol	I_2 absorbed (µg)	absorption time (hours)	I_2 pressure (torr)	I_2 desorbed (µg)	desorption time (hours)	I_2 pressure (torr)
1	o	51.5	~1.5	0.21	3.5	~2.0	0.19
2	◊	67.2	~2.0	0.51	18.1	~5.0	0.43
3	Δ	132.2	~3.0	1.03	69.4	~20.0	0.32
4	▢	131.2	~3.0	0.89	62.7	~18.0	0.28

Data from the desorption measurements.

FIGURE 6

ABSENCE OF HYSTERESIS
IN ABSORPTION ISOTHERM
FOR I_2 IN POLYTHIOPHENE.
SOLID POINTS ARE
MEASUREMENTS DURING
ABSORPTION. OPEN POINTS
ARE MEASURED DURING
DESORPTION.

SOC

PRESSURE I_2 (torr)

MICROMOLES I_2 ABSORBED

equilibrium was defined by the weight which remained constant over a period of many hours. The loss of weight, i.e. the amount of I_2 desorbed in each desorption experiment, is listed in column six of the table.

The first thing to note is the great disparity between the absorption and desorption times. In experiment #4, for example, absorption, commencing with an "empty" film, required only three hours, whereas the desorption of less than half of the absorbed I_2 (only 62.7 of an absorbed 131.2 µg) required 18 hours. In somewhat similar circumstances, in experiment 3, absorption required about 3 hours while desorption required 20 hours. The points for the various experiments are plotted in Figure 6, and can be recognized by the data symbols assigned to them. All the points obtained with desorption appear to lie, within experimental error, on the isotherm obtained by absorption. It would be a remarkable coincidence if this absence of hysteresis were not due to the achievement of reversible thermodynamic equilibrium.

Experiments 1 and 2 are designed to test thermodynamic reversibility within its definition, namely that a small change (reversal) in the thermodynamic state variables should lead to a small, necessary reversal in that state. In experiment 1, the change (reversal) in pressure is only 0.2 torr, i.e. a reversal from 0.21 to 0.19 torr. Experiment 2 involves a slightly larger change of pressure. Nevertheless, as it can be seen in the figure, the isotherm obtained from desorption is essentially identical with that obtained by means of absorption. There is no hysteresis. These experiments, coupled with those described by Figure 5, provide overwhelming evidence that the distribution of the electrically active dopant I_2, between its own vapor and polythiophene, is a reversible thermodynamic process. The disparity between the time for absorption on the one hand and desorption on the other, in no way signals irreversibility.

To prove this point we undertook a theoretical analysis (8) of a diffusant, e.g., a dopant in the presence of "traps" to which it could be bound in instantaneous, but nevertheless reversible equilibrium. (The trapped state could be the ionized state of the dopant in which case it would be fairly strongly bound to the polymer chain.) Thus, along with diffusion, we contemplate the following reversible trapping reaction.

$$A + T \rightleftharpoons AT \tag{2}$$

9

where A is the free diffusant, T the trap, and AT the trapped diffusant. The equilibrium constant $N\alpha$ for this reaction is expressed as

$$\frac{[A] \, [T]}{[AT]} = N\alpha \qquad (3)$$

where N is the total concentration of traps, occupied or not. Thus

$$[T] = N - [AT] \qquad (4)$$

Only free diffusant is able to diffuse, and then with a diffusivity D. The boundary value problem for diffusion in and out of a film of thickness L in the presence of such trapping proved to be quite nonlinear, but could be solved numerically.

For diffusion-in, the boundary concentration of A was denoted as $[A] + [AT] = c_0$. When $c_0 > 1$, i.e., when there can be more diffusant locally than is required to fill all the local traps, there will always be a considerable excess of free diffusant. If a is very small, traps will always be filled locally until only a very small number of unoccupied traps remain, and no diffusion past such a position will be possible until this degree of filling has occurred. Thus the concentration profile is expected to advance as a sharp step, movement of the step taking place when the traps behind it have been filled.

In Figure 7 we show a computed example of such a steplike profile corresponding to $\alpha = 10^{-4}$, i.e., corresponding to very tight binding. Note that ξ and τ are reduced distance and time.

When $c_0 < 1$ there can never be an excess of local diffusant over traps, even when α is very small. Thus the amount of free diffusant allowed by eq 3 will be very small, although larger at smaller values of ξ, where the concentration of total diffusant is larger. Thus diffusion will occur more readily at smaller values of ξ than at larger values. The result will be the accumulation (a backing-up) of diffusant at smaller ξ so that the concentration profile will exhibit a point of inflection. In general diffusion will be slower when α is smaller, since there will be less free diffusant.

In Figure 7 we also show a curve ($\alpha = 10^{-1}$) having the above mentioned point of inflection.

10

FIGURE 7

CONCENTRATION PROFILES OF DIFFUSANT.

DIFFUSION-IN.

$\alpha=10^{-4}, \tau=1$

$\alpha=10^{-1}, \tau=0.1$

$c(\xi, \tau)$

ξ
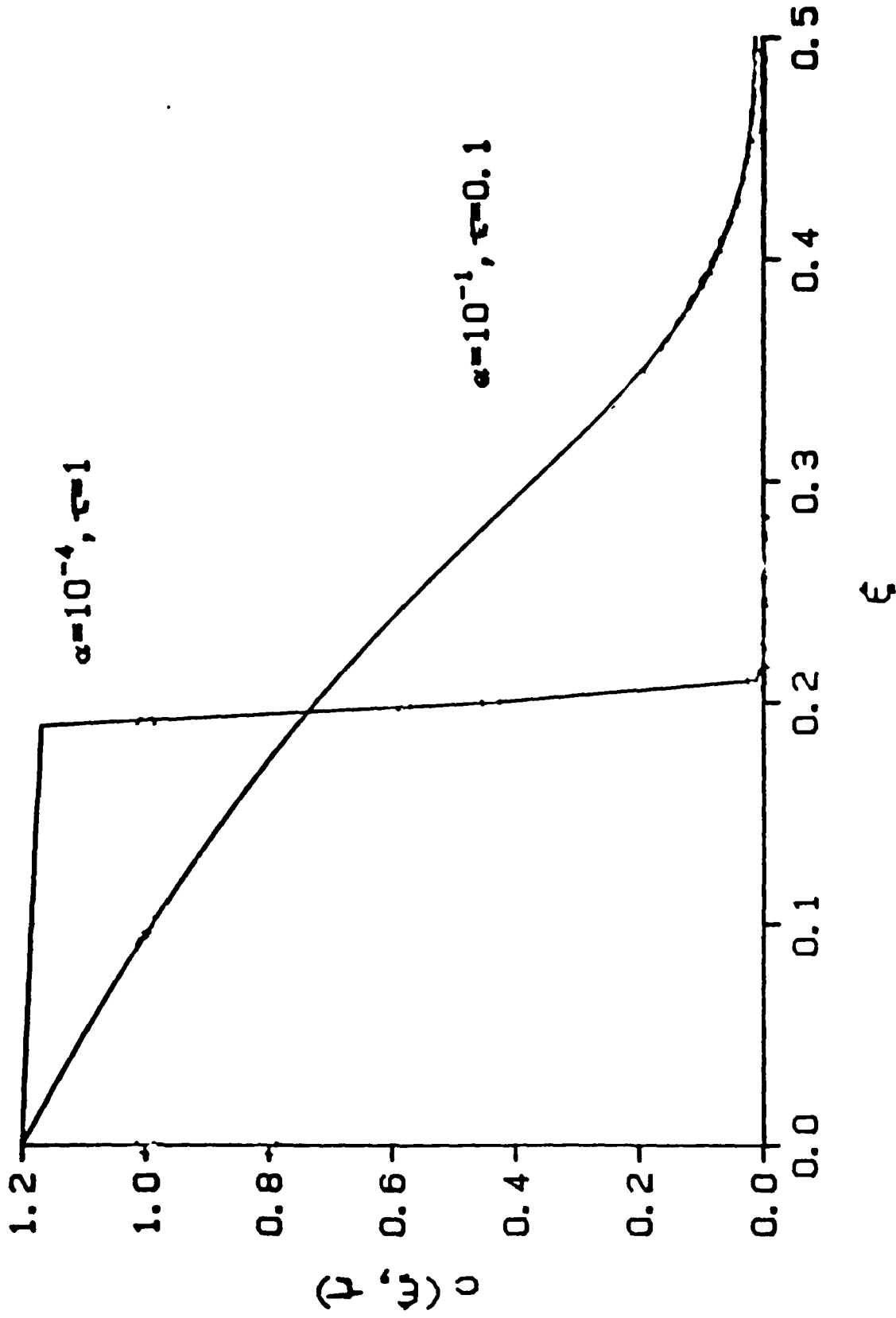
In the case of diffusion-out the region of the film adjacent to its surface will always have a total concentration (free plus trapped) of diffusant, low in comparison to the concentration of traps. As a result, and especially with small values of α, most of the diffusant in the region will be trapped and immobilized. Thus the region will behave as a slowly permeable membrane in comparison to regions at larger values of ξ. To a first approximation, at larger values of ξ, all gradients will have time to level out, so that the only remaining gradient will be a steep one in the slowly permeable zone near the film's surface. The diffusant then "leaks" out in such a manner that the concentration profile is always horizontal behind the slowly permeable zone while its level is uniformly lowered with time in the manner of reservoir behind a dam whose floodgates are slightly opened. Again, in general, diffusion will be slower when α is smaller, since there will be less free diffusant. In general, the times for difusion-out will exceed the times for diffusion-in. The reason for this is the following. Consider first the case where $c_0 > 1.0$. In this case, and for diffusion-in, there is a "perpetual" supply of diffusant at $\xi = 0$ at a level exceeding the number of traps. Thus, even when the traps are filled, there will be free diffusant available to diffuse "over" them. Thus diffusion-in can be relatively fast. On the other hand, even though c_0 initially exceeds the concentration of traps throughout the film, for the case of diffusion-out, since there is only a finite supply of diffusant, its concentration must eventually fall below that of the number of traps. Then, a large fraction of diffusant will be bound and immobilized so that the times for diffusion-out will be relatively long. Thus the disparity between times for diffusion-in and diffusion-out can be explained without involving irreversibility. Direct computation (8) of these times, using the above model confirms these arguments. Figure 8 illustrates some computed profiles for the case of diffusion-out.

Incidentally, diffusion profiles with "steps" such as those appearing in Figure 7 have actually been observed (9) for dopant-conductivity polymer systems.

C.   Electrochemical Studies.

In response to the original objective of this project, i.e., to develop thermodynamically reversible means for the determination of mechanisms and carrier species within a doped polymer, we developed a theory (10) so that "electrochemical doping" could be used for this purpose. Indeed several recent papers (11-16) report experiments in which films of conducting polymers have been examined by means of absorption spectroscopy, conductivity, or potential versus composition, while, at the same time, undergoing electrochemical doping. In one approach (11,12) the pH of the solution bathing the film has

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FIGURE 8
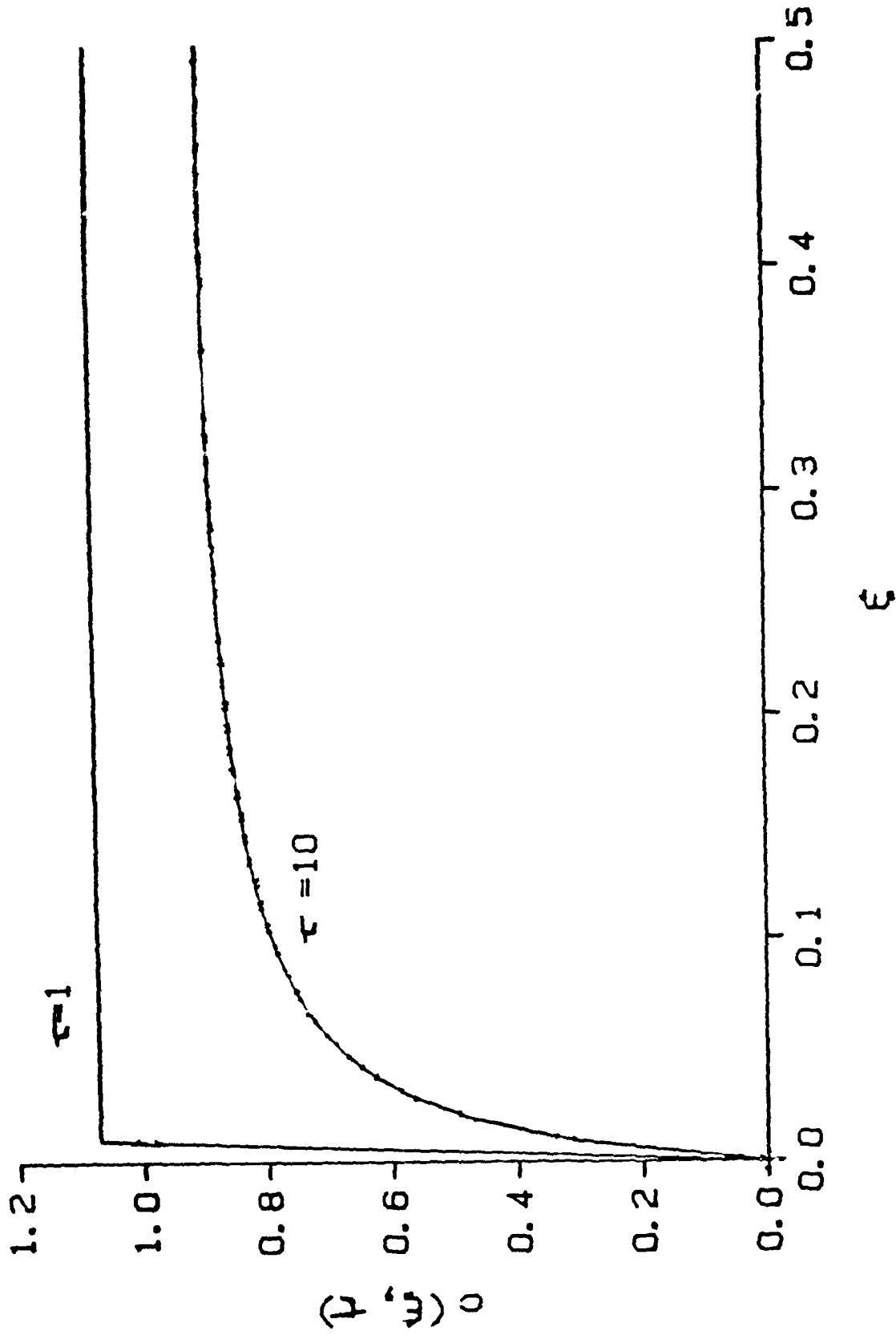
CONCENTRATION PROFILES OF DIFFUSANT.

DIFFUSION-OUT.

been controlled at different levels so as to provide a variable, additional to the optical absorbance used in the interpretation of the several experiments. These experiments, when reversible, can be adapted to the determination of species (polarons, bipolarons, etc.) in the polymer film.

A simple example of this type of system was analyzed. It was composed of an electrochemical cell consisting of a metal electrode M, an electrolyte solution containing the metal cation M^+ and some convenient anion A^-, and a conducting polymer film within which the anion is soluble. For the purpose of measuring the reversible cell potential the film is contacted by a lead wire consisting of M. Assume, for the purpose of this example, that A^- in the film is bound into a "polaron", $A^- \cdot e^+$ where e^+ denotes a positive "hole". Then the strcture of the cell may be denoted, in standard electrochemical notation (10) by

$$M \, |M^+, A^-| \, A^- \cdot e^+, \sigma| \, M' \tag{5}$$

where S and f denote the electrolyte solution and the film, respectively, and the prime on M at the right indicates that the potential of M on this side is different from that on the left. σ denotes a site in the film which is consumed by A^- when it forms a polaron. Assume the cell to be entirely reversible. Then at the first phase boundary (on the left) the following chemical equilibrium is established

$$M(M) \rightleftarrows M^+(S) + e^-(M) \tag{6}$$
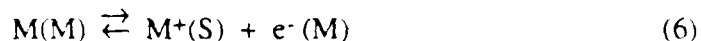
where e^- denotes an electron. The two interfaces on the right support another "chemical" equilibrium, namely

$$A^-(S) + s(f) \rightleftarrows A^- \cdot e^+(f) + e^-(M') \tag{7}$$

It is then shown in reference 10 that the following relation holds,

$$\ell n \, [A^- \cdot e^+] = -K_0 + \ell n \, a_{MA}^S + \frac{eE}{kT} \tag{8}$$

where the square brackets denote concentration, K_0 is a constant, a_{MA}^S is the salt activity in the bathing solution, E is the cell potential, and e is the electronic charge. Now if the

concentration of polarons (or a quantity proportional to it) can be measured by spectral absorbance methods, then according to eq (8) a plot of the logarithm of that quantity versus the applied, *reversible* potential E should exhibit the slope e/kT. Furthermore, if E is maintained constant, while the measurable a_{MA}^S is varied, then, according to eq (8), a plot of $[A^- \cdot e^+]$ versus a_{MA}^S should be linear. When bipolarons $(A^- \cdot e^+)_2$ are present it may be shown that the following relation holds

$$\ell n \, [(A^- \cdot e+)_2] = (2K_o + \ell n \, K_B) + \ell n \, (a_{MA}^S)^2 + 2eE/kT \qquad (9)$$

Similar relations, involving conductivity measurements are also derived in reference 10.

As a critical adjunct to the above analysis, a careful study of the concept of the absolute electrode potential was performed and eventually published (17) as a feature article in the Journal of the Electrochemical Society.

D. Polyaniline

Our research was led into the subject of polyaniline by a paper, due to Chiang and MacDiarmid, (18) on the absorption of protons by emeraldine (semioxidized polyaniline) as a function of pH. Our attention was attracted to this work since Chiang and MacDiarmid were attempting to measure a thermodynamically reversible isotherm. Figure 9a exhibits their original data points (percent proton doping versus pH of the HCl bathing solution) and the curve that they drew through these data without the assistance of theory.

We performed a statistical mechanical analysis (19) (taking cooperativity between absorbed protons into account) of the proton absorption isotherm for this "one dimensional system". The curve derived by means of this theory appears in Figure 9b, and is drawn through exactly the same data points that appear in Figure 9a.

In a more thorough,later investigation Chiang and MacDiarmid concluded that data points 2 and 3 in Figures 9a and 9b were in error while data point 1 was not. Their additional data appear as x's in figure 9c. Note that the curve that they now draw, closely resembles the theoretical curve of Figure 9b. Since the theory is one based on

13

Original data of Chiang and MacDiarmid on adsorption of protons in the emeraldine form of polyaniline as a function of pH
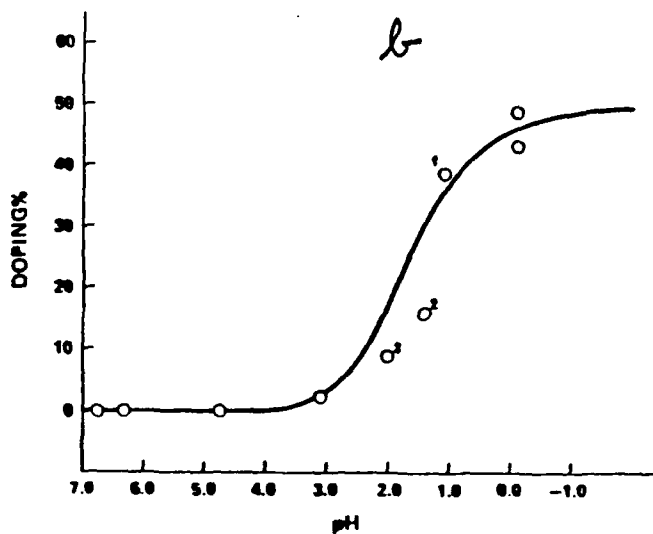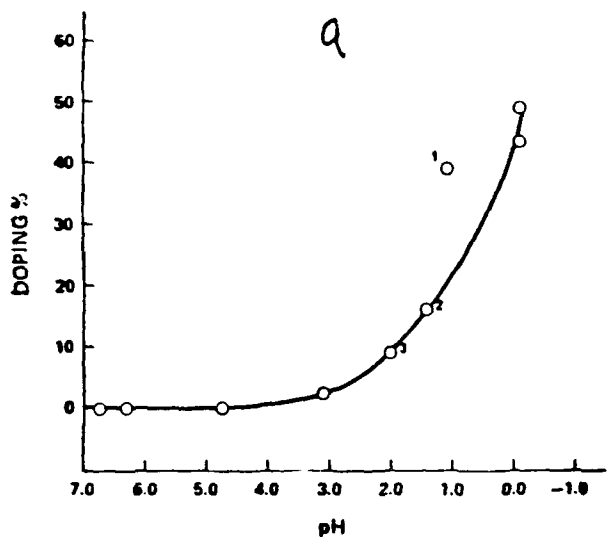
Data points are the same in both figures, but the left figure shows the original curve drawn by Chiang and MacDiarmid while the right figure shows the curve drawn from transfer matrix theory, taking cooperativity into account.

X's are new data

of Chiang ⟶ and MacDiarmid. Circles are old data
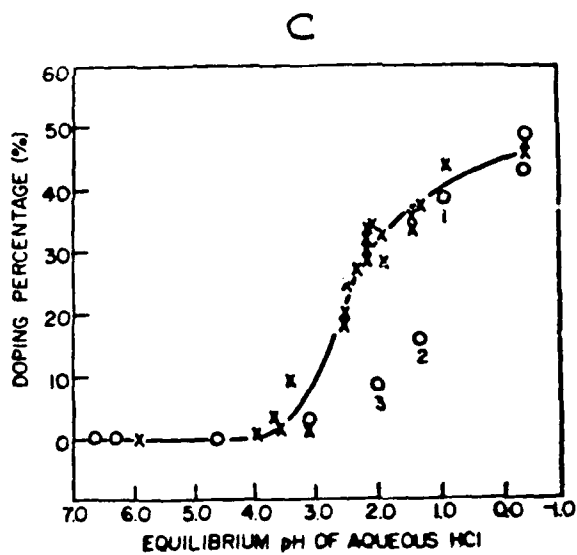
Curve is the new curve

⟵ Drawn by Chiang and MacDiarmid.

FIGURE 9

thermodynamic equilibrium, such agreement suggests that the emeraldine-proton system is another example of the achievement of thermodynamically reversible equilibrium.

Efforts to establish the thermodynamically reversible nature of the curves in Figure 9 led to attempts on the part of MacDiarmid's group to demonstrate the absence of hysteresis in such isotherms measured during desorption as well as absorption. In a typical experiment, emeraldine was saturated with protons by immersion in an aqueous solution of HCl, and then protons were removed by the addition of aqueous NaOH. Careful consideration of these experiments reveals that upon desorption the bathing solution must contain NaCl as well as HCl, so that at a given pH its ionic strength exceeded that of pure aqueous HCl at the same pH. This should give rise to a Donnan equilibrium like distribution of protons between the bathing solution and the polymer so that apparent hysteresis should occur even though true thermodynamic equilibrium may have been established.

As a consequence, in collaboration with MacDiarmid's group, we developed a theory for the "modified" Donnan equilibrium involved (20).

The most conventional example of the "Donnan equilibrium" involves an ion exchange resin or membrane bathed in an aqueous solution containing a single electrolyte, e.g. NaCl. If the fixed ions (attached to the resin structure) are anions, e.g. sulfonic acid groups attached to polyethylene, then when ion equilibrium between the bathing solution and the resin is achieved there will be a higher concentration of electrolyte cations (Na^+ in the case of NaCl) in the resin as counterions than in the solution. The electrolyte anion will be the coion and will normally enter the resin in low concentration. An electrical double layer will also develop at the interface between the resin and the solution so that a built-in electric field will form, having a direction such as to drive the fixed ions out of the resin if they were not anchored. The potential associated with the field is the well known Donnan potential. An interesting new situation arises if the fixed ions are not bound infinitely strongly to the resin, i.e. if they are slightly dissociated or possess a small dissociation constant. Then the built-in field, since it acts to drive the fixed ions out of the resin, will tend to enhance this dissociation, and anything that reduces the field intensity, i.e. reduces the Donnan potential will tend to suppress the dissociation. One way to accomplish this is to increase the ionic strength of the bathing solution. The additional ions (of both signs) made available by such an increase will act to "screen" the electric field and reduce the double layer potential. Indeed, this effect is already known in connection with the ordinary Donnan equilibrium where the ion selectivity (high concentration of counterions in the resin) can be nullified

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when the concentration of ions in the bathing solution far exceeds the concentration of fixed ions in the resin.

A real example of a resin possessing dissociable fixed ions consists of the protonated form of emeraldine, the semioxidized derivative of the remarkable conducting polymer, polyaniline. In this case the protons, strongly bound to emeraldine, are the dissociable fixed ions. Thus the fixed ions are now cations rather than anions, while the counterions are cations.

Emeraldine base is normally protonated by bathing it in hydrochloric acid solution. The degree of protonation depends on the pH of the acid solution, a greater degree of protonation being achieved when the solution is at lower pH. From what has been suggested above, however, the degree of protonation should be increased, at fixed pH, by increasing the ionic strength of the solution through the addition of a salt such as NaCl. This should act to screen the double layer field, and reduce the Donnan potential so that it provides less aid to the process of proton dissociation. The net result will be an increase in the equilibrium level of protonation without an increase in pH.

Our theory for this modified Donnan equilibrium leads to the following relation

$$n_1 = \frac{N p_2^2\, p_1\, (N - p_2) - A p_1^3\, (N - p_2)^2}{A p_1^2\, (N - p_2)^2 - B N^2 p_2^2} \tag{10}$$

where N is the concentration of proton absorbtion sites in emeraldine, p_1 and p_2 are the proton (hydrogen ion) concentrations in the bathing solution and polymer, respectively, while n_1, is the concentration of sodium ions in the bathing solution and A and B are constants. The degree of proton absorption, measured by p_2, can be obtained as a function of pH, ($- \log p_1$) and NaCl concentration n_1, by solving eq (10) for p_2.

In the special case that the proton uptake p_2 is small compared to N, the solution for p_2 in eq (10) can be well approximated (using $N - p_2 \approx N$) by

$$p_2 = p_1 \left\{ \frac{A(n_1 + p_1)}{B n_1 + p_1} \right\}^{1/2} \tag{11}$$

15

which, upon using the definitions of A and B provided by the theory can be further modified to yield

$$p_2 = K_p (K_r/K_n)^{1/2} p_1 \left\{ \frac{n_1 + p_1}{n_1 + (K_p/K_n) p_1} \right\}^{1/2} \tag{12}$$

where the K's are also constants.

This is a convenient analytical expression for the dependence of p_2 on both n_1 and p_1. The theory shows that (K_p/K_n) is a very large number. As a result the numerator in curly brackets, in eq (12), increases more rapidly (at fixed p_1) with n_1 than the denominator. This means that p_2, prescribed by the equation increases with n_1, revealing the effect we have been discussing, namely that proton adsorption is <u>increased</u> by an increase of the salt concentration in the bathing solution!

The Donnan potential $\varphi = V_2 - V_1$, i.e. the equilibrium potential difference between the polymer and solution phases, can also be calculated from the theory. It proves to be

$$\varphi = \frac{kT}{e} \ln \left\{ \frac{K_p p_1}{p_2} \right\} = \frac{kT}{2e} \ln \left\{ \left(\frac{K_n}{K_r} \right) \left(\frac{n_1 + (K_p/K_n) p_1}{n_1 + p_1} \right) \right\} \tag{13}$$

This equation shows that φ is reduced by an increase in n_1, i.e. by increasing the salt concentration of the bathing solution. This is the effect mentioned above.

Experiments have been performed in MacDiarmid's group to test the effect predicted by the theory for the modified Donnan equilibrium. Indeed, the proton uptake, by emeraldine is found to increase in the presence of NaCl, i.e., with increased ionic strength of the bathing solution.

Preliminary data is plotted in Figure 10. The shape of this curve is consistent with theory.

Again, in collaboration with the Pennsylvania group, we looked into the theory of another interesting equilibrium phenomenon involving polyaniline. This concerned the nature of an isobestic point in the spectrum of a solution containing both leucoemeraldine and

DONNAN EFFECT ON
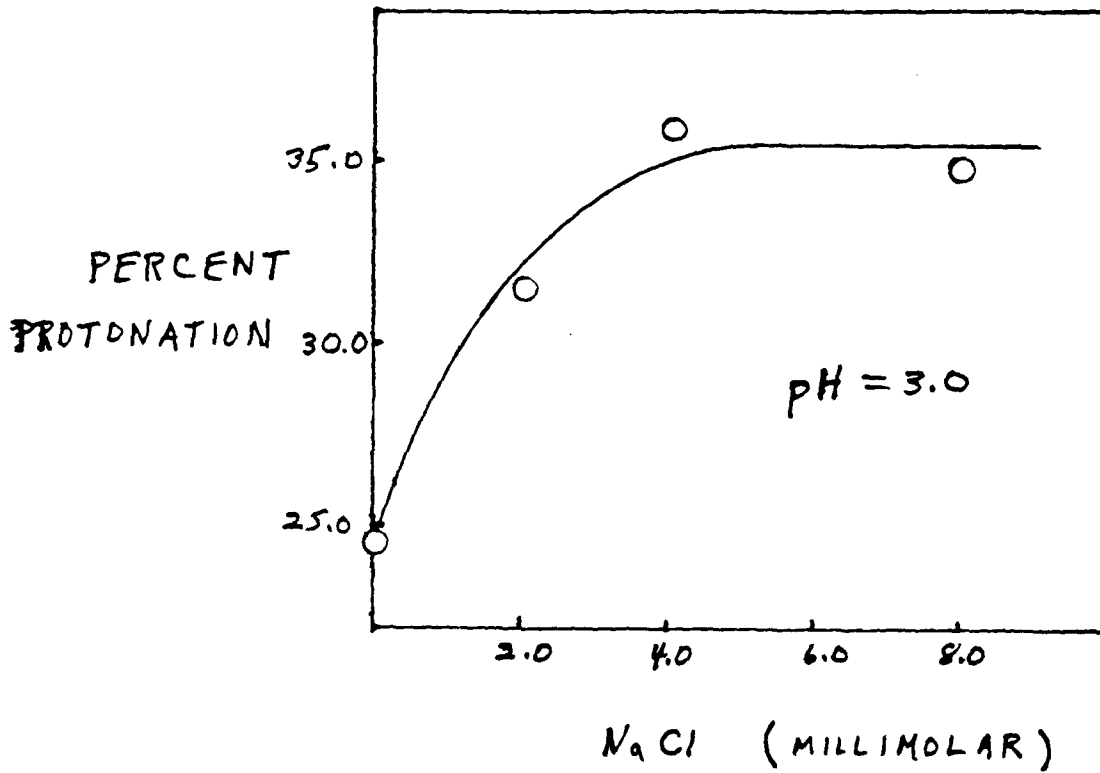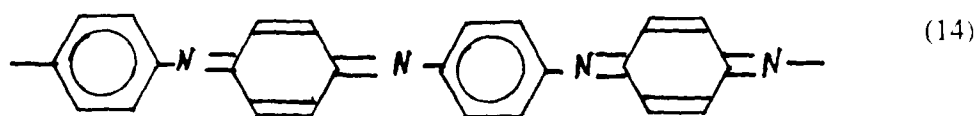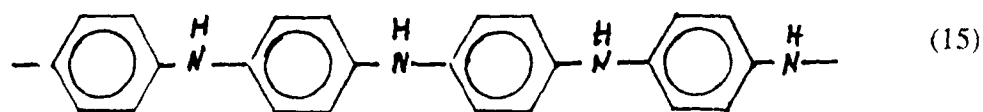PROTON ABSORPTION
BY EMERALDINE

FIGURE 10

pernigraniline dissolved in NMP. Apparently an internal redox reaction between the two polymeric solutes takes place.

When pernigraniline is added to leucoemeraldine dissolved in NMP, the absorption, in the range 260 nm to 900 nm, is observed to shift in the manner illustrated in Figure 11.
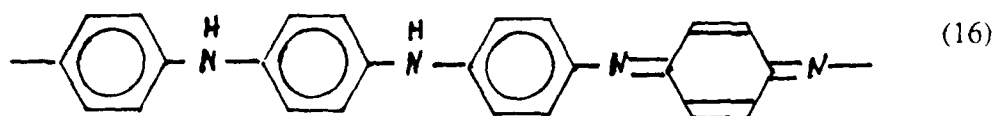
The spectra labeled 1,2,3, etc. in Figure 11 correspond to increasing addition of the fully oxidized polymer (pernigraniline), and the intersection indicated by I represents an excellent isobestic point. What can be learned from it, i.e. how can it arise. Pure pernigraniline (fully oxidized polymer) has the following structure

$$-\left\langle\bigcirc\right\rangle- N=\left\langle\bigcirc\right\rangle= N -\left\langle\bigcirc\right\rangle- N \equiv \left\langle\bigcirc\right\rangle \equiv N- \qquad (14)$$

which we denote as species B. Pure leucoemeraldine has the form

$$-\left\langle\bigcirc\right\rangle-\overset{H}{\underset{N}{}}-\left\langle\bigcirc\right\rangle-\overset{H}{\underset{N}{}}-\left\langle\bigcirc\right\rangle-\overset{H}{\underset{N}{}}-\left\langle\bigcirc\right\rangle-\overset{H}{\underset{N}{}}- \qquad (15)$$

which will be designated as species A. Finally, emeraldine has the form

$$-\left\langle\bigcirc\right\rangle-\overset{H}{\underset{N}{}}-\left\langle\bigcirc\right\rangle-\overset{H}{\underset{N}{}}-\left\langle\bigcirc\right\rangle- N=\left\langle\bigcirc\right\rangle= N- \qquad (16)$$

which we denote as species C.

With these definitions $\underline{any}$ polymer, intermediate to A and B might have the form

-AAAABABBAAABBBBA-   (17)

etc.

Note that we have $\underline{specifically}$ designated the three species as consisting of $\underline{four\ ring}$ chains. Why did we not choose two ring chains, a practical option for both A and B? The answer lies in the requirements of C which cannot be represented by any number of rings less than four. Indeed, if two ring chains were to be used, C would not be a new product, but would consist only of A and B. The same comment would apply to the intermediate structure in eq (17).

17

FIGURE 11

Constant luco. concentration vary (increase) pernig. conc.

ILLUSTRATION OF ISOBESTIC
POINT IN SPECTRA OF
SOLUTIONS OF LEVCOEMERALDINE
AND PERNIGRANILINE IN
NMP.

ABSORBANCE

WAVELENGTH (nm)
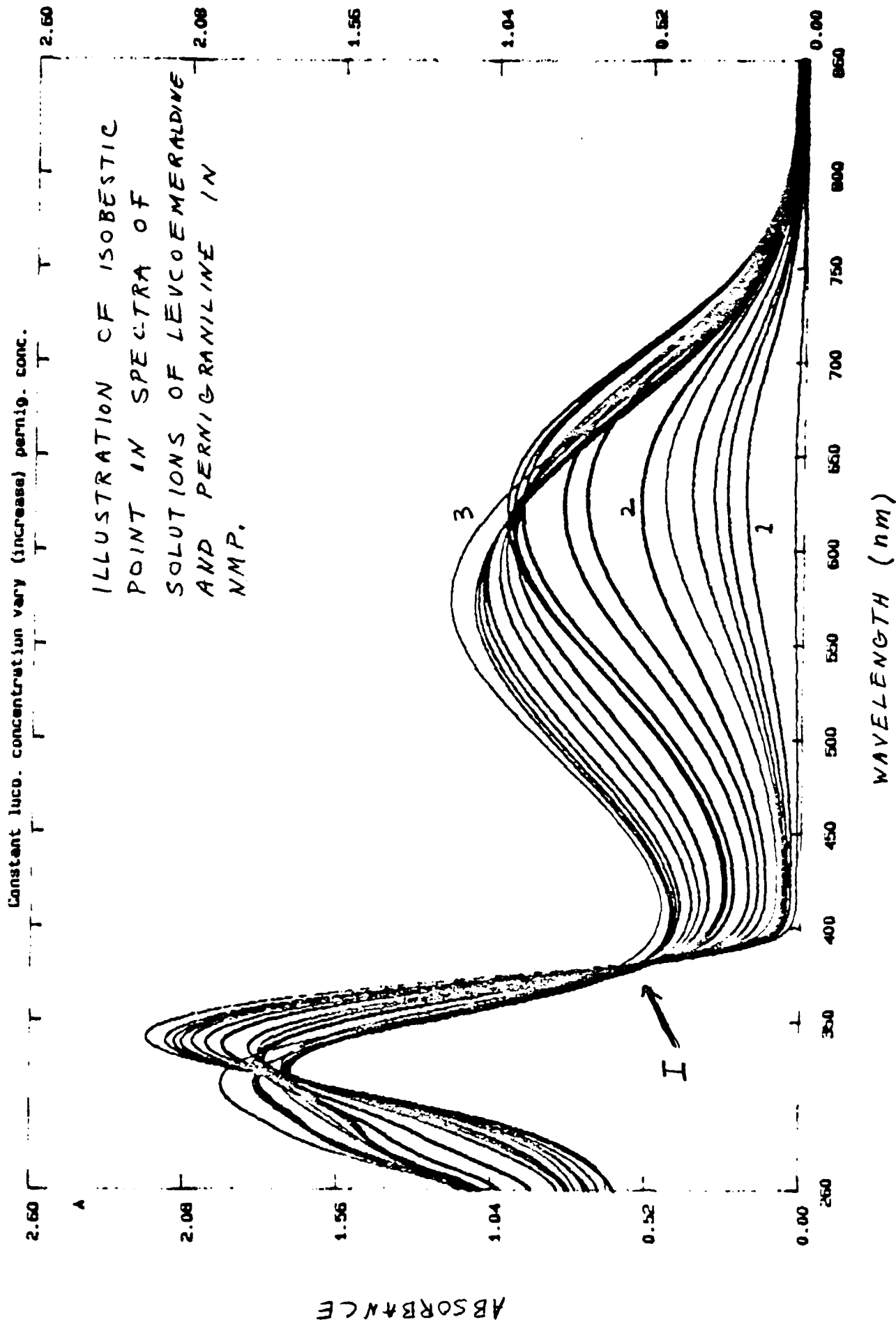
We want to able to assign a characteristic absorption spectrum to C. If, in each case, the spectrum was determined by two ring chain, then the spectrum of C, and for that matter the species in eq(17), would be nothing more than a weighted superposition of the spectra of A and B, and, even if A and B participated in the following reaction,

$$A + B \rightarrow 2C \tag{18}$$

(a stoichiometric possibility) the reaction would not change the spectrum at any wavelength, i.e. every point in the spectrum would be isobestic! Clearly, this is not the case, and therefore the fundamental units must exceed two rings in size.

How long does each species have to be before it yields a spectrum, invariant to length? There is some evidence that it must contain at least eight rings. When A is mixed with B therefore, if the resulting structures due to the reaction in eq (18) are of the form,

$$AAABBCCCCAABBBBCC\ldots \tag{19}$$

etc., the spectrum will appear to consist of the weighted superposition of three spectra. On the other hand, sequences such as

$$AAABCCCCABBBBCBB\ldots \tag{20}$$

will have more complex spectra, since they include runs of only four rings (the single B, A, and C , etc.).

If there are three species having extinction coefficients $\in_A$, $\in_B$, and $\in_C$, then the first requirement for an isobestic point is that their individual spectra must overlap partially or intersect. $\in_A$, $\in_B$, and $\in_C$ each depend on wavelength, but in order to have an isobestic point, there must be a wavelength at which $\in_A$, $\in_B$, and $\in_C$ must be in special relation.

A second scheme for maintaining W constant is less demanding. We assume that eq (18) is reversible so that chemical equilibrium is established, i.e.,

$$A + B \rightleftharpoons 2C \tag{21}$$

18

However, we also assume that the equilibrium is so much in favor of the product C that virtually all of the added B is consumed. Then it may be shown (21) that if at a particular wavelength λ

$$\in_A (\lambda) = 2\in_C (\lambda) \tag{22}$$

An isobestic point will occur at that wavelength.

This theory predicts many other things and even contains the methodology for studying cooperativity along the conducting polymer chains. It also allows one to extract the individual values $\in_A$, $\in_B$, and $\in_C$ from the data on mixtures at any wavelength. The theory also predicts that there should be a break in the absorbance curve (absorbance versus pernigraniline added to leucoemeraldine) when leucoemeraldine and pernigraniline are in equimolar ratio in the solution. Furthermore, each portion of the absorbance curve should be linear. The experimental data, exhibited in Figure 12, support this prediction.

E. Rectification in Macroscopically Uniform Conductors.

Collaboration with the Pennsylavnia group resulted in an interesting theoretical study (21) of the effects of microscopic fluctuations in the properties of conductors on bulk conductivity even when the bulk properties appeared uniform. For example, four point probe measurements aimed at determining the resistivities of conducting polymers, often yield different resistivities in opposing directions. Such disparities, when they are small, can be due to instrumental problems or to temperature gradients leading to a Seebeck potential. However, they might also be due to intrinsic conformational problems (or doping problems) resulting from either the method of polymer preparation or to the mechanical treatment of the polymer (e.g. the introduction of strain). We examine the features which can give rise to such intrinsic effects.

Under what conditions can a conducting material exhibit different resistivities in opposite directions. This phenomenon is common at a junction between two materials (rectifying contact) or for example at a p,n-junction in a semiconductor. Both cases are characterized by the presence of "gradients" of charge carriers. For example, at a contact, the bulk concentrations of carriers are different in the two materials, and at a p,n-junction the concentrations of electrons and holes change precipitously as the junction is penetrated. Indeed, the fundamental reason for rectification in these structures is that when a potential is
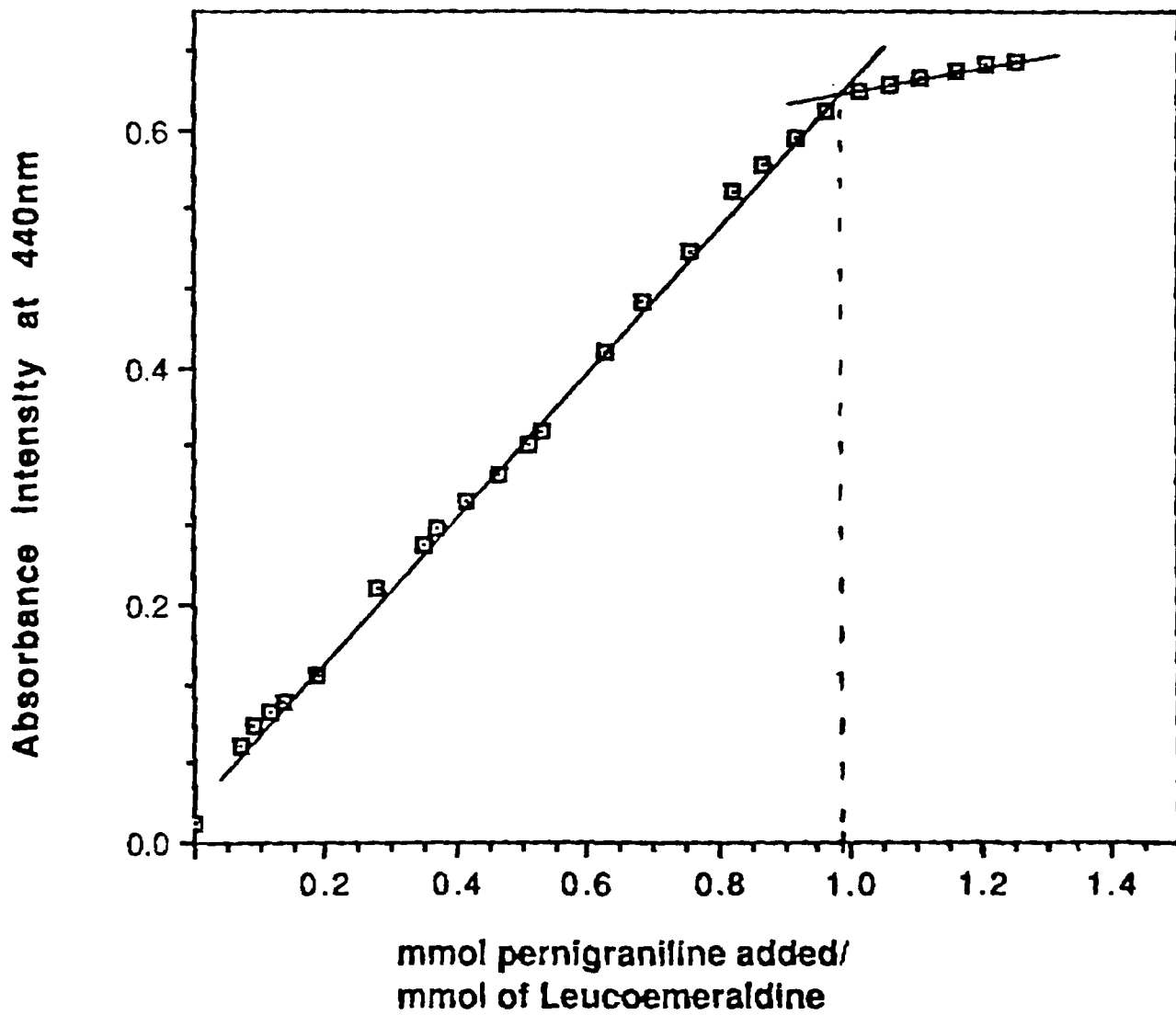
19

FIGURE 12

applied, such that carriers are driven "up" the gradient, one draws them from an "impoverished" reservoir and sends them to a "rich" reservoir. Under this condition carriers are difficultly available and, as a result, little current flows. When the potential is applied in the opposite direction, carriers are withdrawn from the rich reservoir and sent to the poor one so that a large current can be sustained. Clearly this is the "forward" direction of the rectifier while the opposite is the reverse direction. Equally clearly, the carrier gradient is fundamental to the rectification.
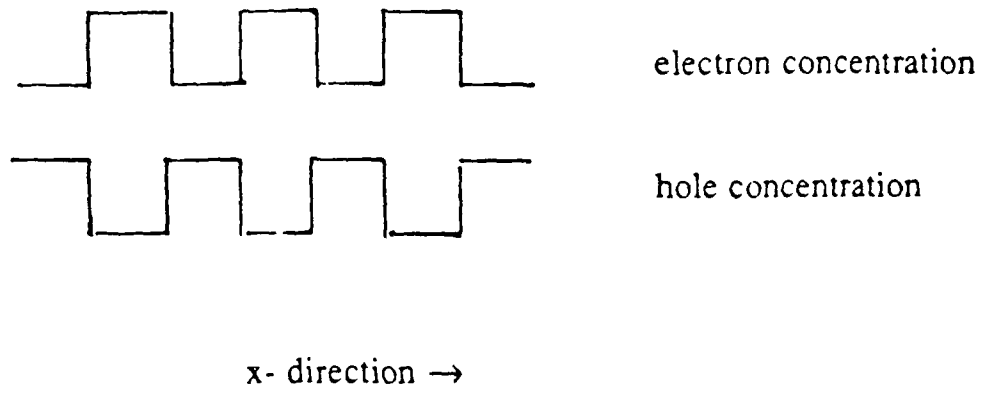
Is it possible to have a distribution of gradients on a "microscopic".scale that can lead to rectification, but which also present a "uniform" appearance (i.e. no gradients) on a "course grained" "macroscopic" scale? One possibility would be a sequence of p, n-junctions parallel to, say the x-direction, so that the dopant levels would present the profiles in Fig. 13a. Over a long enough interval, in the x-direction, the "average" concentrations of both electrons and holes would exhibit no gradient. Unfortunately, however, there would also be no rectification - only high resistance - because alternate junctions would always be "reversed" no matter what the direction of the applied potential. However, a relaxing of the profiles in Figure 13a to the distribution in Figure 13b would solve this problem.

In this structure a reasonably large current could flow in the positive x direction and only a small current in the negative direction, and yet the "average" concentrations of carriers over a long enough distance would be constant. Corresponding to Figure 13b the "net" electron concentration (electrons minus holes) would be as in Fig. 13c. In this figure the horizontal line represents the level of zero "net" doping and the circles therefore mark the locations of p, n-junctions. The junctions with the more gentle doping gradients are poorer rectifiers so that when they are reverse biased they do not exhibit the high resistivity of the alternate "step" junctions which are "reversed" when the gentler junctions are forward biased. Thus the system exhibits different resistivities in opposite directions.
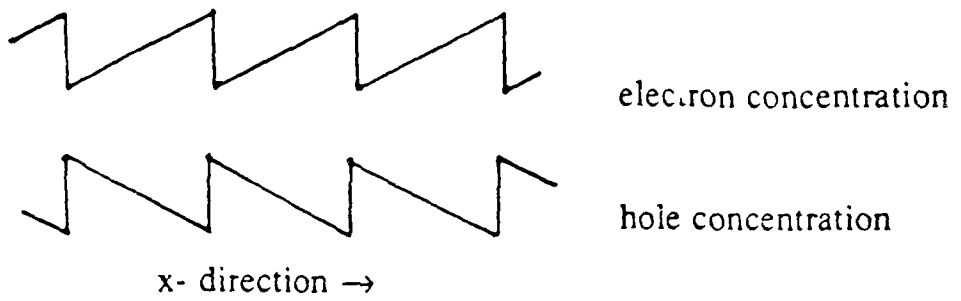
Having presented this example of "rectification" in the absence of macroscopic carrier gradients, it is of interest to examine the question in a more general way. For this purpose consider a conducting medium, e.g. a semiconductor or a conducting polymer where the doping level fluctuates with position, although again, we assume that on a macroscopic level the doping remains uniform, i.e. there are no gradients. In the absence of an applied field, the carrier concentration will fluctuate with the dopant. The medium need not be a dopable semiconductor or polymer; all that is necessary is that the carrier concentration and its fixed counter charges (e.g. ion cores in a metal) exhibit fluctuations in concentration.

20

NO RECTIFICATION

electron concentration

q

hole concentration

x- direction →

b

elec:ron concentration

hoie concentration

x- direction →

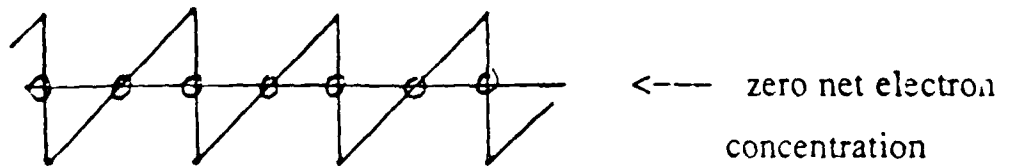RECTIFICATION

C

<--- zero net electron

concentration

FIGURE 13

The equations governing the conductive and voltaic behavior of the carriers in this medium are the well known Nernst-Planck equation, and the Poisson equation. These are

$$J = -qD \frac{dc}{dx} - \frac{q^2 D}{kT} c \frac{dV}{dx} \tag{23}$$

and

$$\frac{d^2 V}{dx^2} = -\frac{4\pi q}{\kappa} [c(x) - N(x)] \tag{24}$$

Eq(23) is the Nernst-Planck equation. In it J is the electrical current density (charge per unit area per unit time--e.g. coulomb $cm^{-2} sec^{-1}$) and q is the charge (positive or negative) on a carrier. $c(x)$ represents the concentration of carriers at position x, $V(x)$ is the electrical potential at x, D is the diffusion coefficient of a carrier, κ is the Boltzmann constant, and T is the temperature.

Eq (24) is Poisson's equation. In it, $N(x)$ represents, the "possibly" fluctuating concentration of fixed counter charges, e.g. of dopant ions, while κ is the dielectric constant of the medium. Eqs (23) and (24) are basically continuum equations and involve several approximations which we will not discuss in detail, since their effects are of little consequence to the problem at hand. In any event the equations have found broad use in both electrochemistry and semiconductor device theory.

Analysis (21) of the symmetry properties of eqs (23) and (24) allows one to establish the types of microscopic fluctuations under which rectification can occur even though the conductor appears to be macroscopically uniform. Figures 14a and 14b illustrate two possible forms for a microscopic variation of the doping level $N(x)$. In Figure 14a, the pattern has no reflection symmetry in a plane normal to the x axis. The total $N(x)$ is indicated by the solid wavy line, while the dashed line, at unit elevation, is meant to indicate the value, of N_0, the uniform average concentration. The example in Figure 14a shows periodic fluctuations, but there is no need for the distribution to be periodic. The fluctuations are shown as small compared to unity, but there is no need for this, either. Indeed Figure 13b exhibits a case (still periodic) where the fluctuations are large.
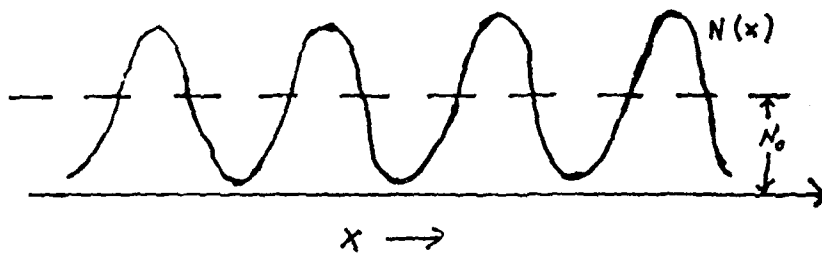
Figure 14b exhibits a case in which there is reflection symmetry and where fluctuations are large. Figure 13a provides another example. In both Figures 14a and 14b the macroscopic average concentration is independent of x.

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ABSENCE OF REFLECTION SYMMETRY
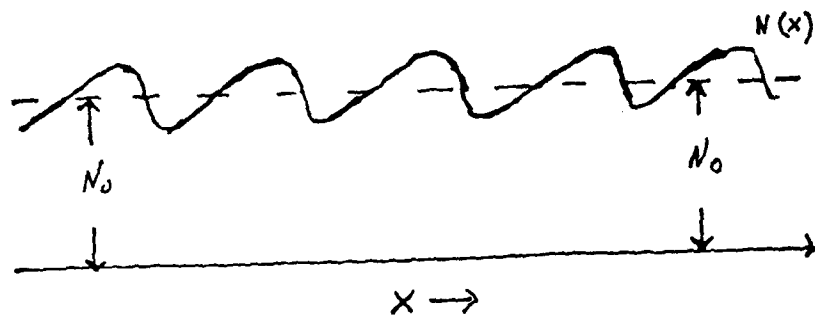
REFLECTION SYMMETRY

FIGURE 14

It is reasonable to expect that rectification will not occur when $N(x)$ possesses reflection symmetry, as in the case of Figure 14b. This can be established (21) by examining the symmetry properties of eqs (23) and (24). When reflection symmetry in $N(x)$ is absent, on the other hand, rectification might be expected, and this too has been established from the symmetry properties of eqs (20) and (21).

In general, reference (21) demonstrates the following facts, applying to rectification and nonrectification in conductors in which the equilibrium dopant concentration may fluctuate on a microscopic level, but not on the macroscopic level:

1) If there are no fluctuations in dopant concentration, the system will not rectify.

2) If the fluctuating distribution of dopant concentration possesses reflection symmetry, the system will not rectify.

3) If the fluctuating distribution of dopant concentration does not possess reflection symmetry, then rectification will occur, except for certain rare distributions in which almost miraculous compensations may occur.

Note that nonsymmetrical distributions (although not necessarily periodic), of the type illustrated in Figure 14a, may occur in conducting polymers due to either the mode of preparation or mechanical treatment after preparation. Thus rectification, in the absence of bulk gradients, could occur in such polymers. Such rectification will be small if the underlying fluctuations in dopant density are small.

Another interesting question deals with the possibility that, due to a possible, unsymmetrical carrier scattering mechanism, a conductor, not having dopant fluctuations even on the submicroscopic "molecular" level, can exhibit rectification. An analysis (23) using the Boltzmann transport equation proves that rectification, in such systems is impossible without violating the principle of microscopic reversibility.

F.   Conducting Polymer Films as Gas Selective Membranes

As indicated at the beginning of this report, studies are in progress to characterize conducting polymers as gas selective membranes.

TABLE 2

SEPARATION RATIOS

	He/N_2	O_2/N_2	CO_2/CH_4
EM^*	3500	50	36
PTFC	2200		
CELLULOSE NITRATE		16	
F-POLYIMIDE			60

FILMS

Our initial entry into this field was motivated by the possibility of depositing a thin layer of metal (~ 20 nm) on one surface of a conducting polymer film (see Figure 15), and, in so doing, produce a Schottky junction at that surface. Gas would then be made to diffuse through the uncovered surface of the film, normal to it and ultimately out through the metal layer as indicated in Figure 15.

As is also indicated in Figure 15, an electrical double layer exists at the junction. Attraction between the oppositely charged, anchored layers can cause a compressive stress (within the thin space charge layers) of between several hundred thousand to one million atmospheres. Furthermore the layers can be modulated by the application of an externally applied potential V as illustrated in Figure 15.

The original idea was to develop an "active" as opposed to a "passive" gas selective membrane in which one could tune to the separation of a particular gas by varying the applied potential (≈ 1.0 volt) in reverse bias. The solubility of the gaseous diffusants in the high pressure layer could be modified by the high pressure, and modified differently for different species so as to favor the permeation of one of them. Furthermore, the large inhomogeneous electric field should favor the transport of the more polar molecule. Finally, the relatively low modulus of elasticity of the film should result in considerable compressive strain. All of these factors represent "handles" in the control of separation.

The fabrication and study of such an active membrane is still planned, and we have already studied the gas permeation through the thin, deposited layer of metal, however, along the way, it was discovered that a film fashioned from the emeraldine form of polyaniline (with hardly any attempt at optimization) already outperformed all films in the published literature (4) in the selective separation of hydrogen, helium, and oxygen from nitrogen. The most effective film was prepared by first saturating emeraldine film with protons by immersing it in aqueous HCl. Following this step, the protons were removed by immersion in ammonium hydroxide. The final film, denoted by Em*, is compared with the "best" published films in Table 2 where the entries in the matrix represent the separation ratios listed in the row at the top of the matrix. The films are listed in the column to the left of the matrix. The films are all "passive"; no Schottky junctions were involved.

Note, from Table 2, that Em* separates helium from nitrogen at a ratio of 3500 to 1.0 while oxygen is separated from nitrogen at a ratio of 50 to 1.0. In the published literature (4) the nearest competitors are KelF which separates helium form nitrogen at a ratio of only

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An "active" gas selective membrane
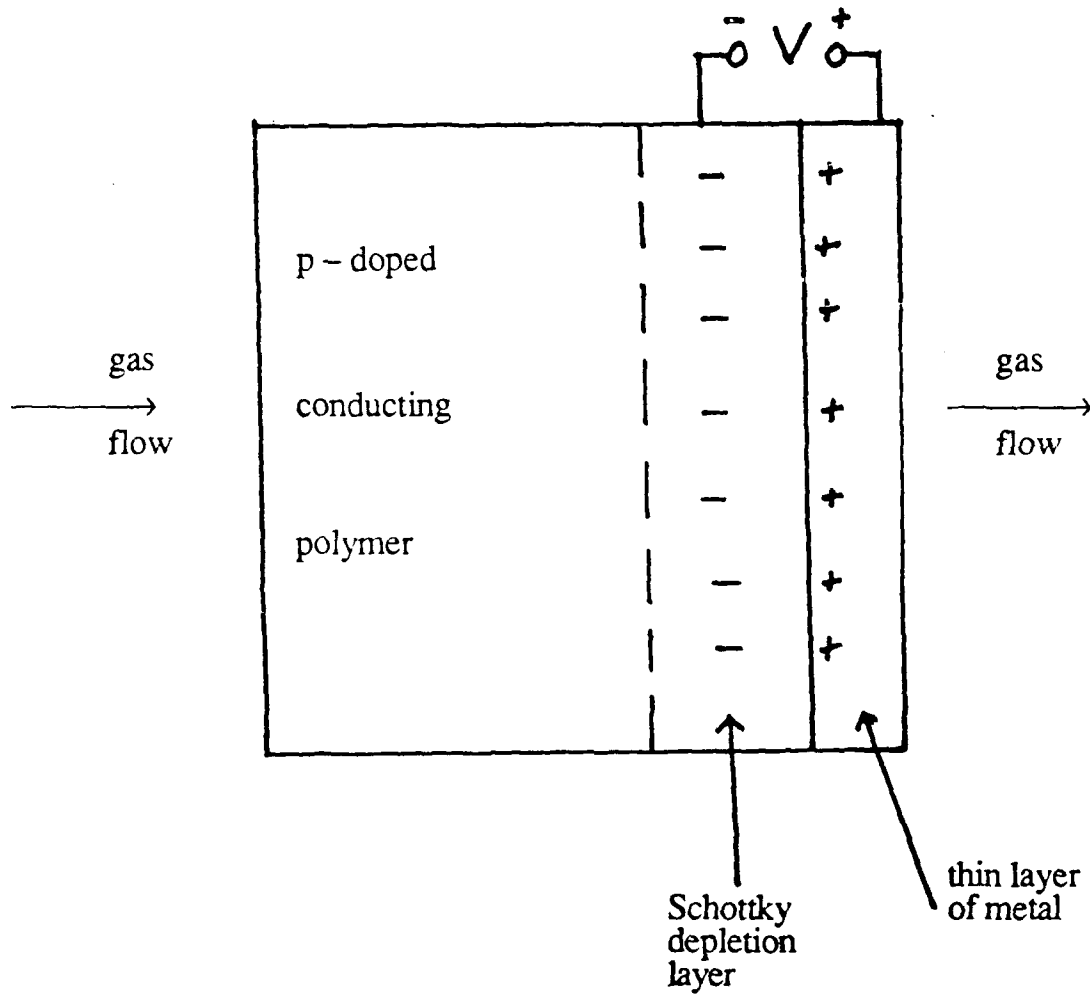
Application of a reverse bias potential (V ~ 1.0 volt) leads to a large increase in internal electric field and to a large compressive strain. "Tune" to the selection of a particular gas.

FIGURE 15

2200 to 1.0 and cellulose acetate which separates oxygen from nitrogen at a ratio of only 16 to 1.0. Furthermore Em* separates both species in high ratio while two different films are required in order to achieve high respective ratios for helium and oxygen.

There is a large number of variables that can be controlled and changed in order to achieve optimization in the case of conducting polymer films. The fact that such excellent performance has been achieved with hardly any optimization indicates that conducting polymers may be the best gas selective membranes. Furthermore they offer the opportunity to produce "active" membranes.

As already indicated a collaborative effort is already under way with the University of Pennsylvania group, in order to exploit these possibilities, and membrane test apparatus has been constructed for that laboratory.

In addition, UCLA is in the process of making a patent disclosure (24).

IV. Closing Remarks

As can be seen from the above, considerable progress has been made in addressing the original objectives of the contract, and, during the course of research, additional objectives have been formulated and pursued. This effort has also been met with some success. Further research into these areas will be pursued when funds become available.

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