pounds. This situation is certainly not the case. Other strong interactions that could be influencing nitroaniline packing patterns are charge transfer interactions and dipole–dipole interactions. No systematic structural analyses of the effects of charge transfer on the packing of nitroanilines has been reported, but two groups have analyzed the role of dipole–dipole interactions on the packing of polar molecules in organic crystals.[9,10] These studies are important here since most nitroanilines are also polar molecules. Interestingly, our analyses show that 20% of tertiary nitroanilines, where hydrogen bonds are not present to compete with dipole–dipole interactions, form noncentrosymmetric structures. This percentage is very close to that found by Gavezzotti for his prototype dipolar molecules (monosubstituted carbonyl and nitrile compounds) for which about 20% are found in $P2_12_12_1$ and $P2_1$ noncentrosymmetric space groups[9] (Table IV). An interesting future project would be to carry out a dipole moment/space group correlation on the sets of nitroaniline structures presented here to see if the dipolar contribution to noncentrosymmetry can be separated from the hydrogen-bond contributions.

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Conclusion

We have found that while achiral organic molecules in general have an 11% chance of forming noncentrosymmetric crystal structures, achiral nitroanilines that have single $-NO_2$ and $-NH_2$ (or $-NH$) groups and that form hydrogen-bonded chains have a 46% chance of forming noncentrosymmetric structures. We interpret this high incidence of noncentrosymmetric structures in this class of compounds as an indication that noncentrosymmetric hydrogen-bonded aggregates induce noncentrosymmetryity during crystal nucleation. If this interpretation is correct, it implies that choosing molecules with hydrogen-bonding groups that drive molecules to aggregate into chains are useful for improving one's chances of obtaining noncentrosymmetric crystal structures, even for achiral molecules.

Acknowledgment. This work was supported by the Office of Naval Research. We are grateful to Profs. Wnek (Rensselaer Polytechnic Institute) and Lechat (University of Sao Paulo) and Drs. Stiegman (JPL Laboratory) and Twieg (IBM) for crystal structure data on as yet unpublished results.

Supplementary Material Available: Structures with R factors between 11% and 16%, CSD search algorithms, and the search results with Refcodes and bibliographic citations (13 pages). Ordering information is given on any current masthead page.

Fluorescence Anisotropy as a Probe of Molecular Mobility in a Plasticized Poly(vinyl chloride) Membrane

Yangzhen Ciringh,† Michael Del Rosario, and Stuart L. Belli*

Department of Chemistry, Vassar College, Poughkeepsie, New York 12601

Received December 10, 1991. Revised Manuscript Received March 24, 1992

Steady-state fluorescence anistropy is shown to monitor the mobility of a small molecule in a plasticized polymer membrane and yields information about the microviscosity in the membrane. The technique was applied to a valinomycin based neutral-carrier K^+ ion-selective electrode and a relationship was derived expressing the bulk resistance of the membrane in terms of the microviscosity. The bulk resistance was then measured by ac impedance and shown to correlate with the microviscosity verifying the derived relationship. The instrumentation is described, including a discussion of the anisotropy calculation for measurement from a planar membrane held at a fixed angle in the light path. The results of experiments carried out on the valinomycin electrode suggest that the K^+–valinomycin complex is the mobile, charge-carrying species in the membrane.

Introduction

The study of ionic conduction in neutral-carrier ion-selective electrodes has relied primarily on ac impedance to measure electrical resistance through the bulk of the membrane. This information is important for understanding the identity of the charge-carrying species and the mechanism of charge movement. It would be useful to monitor the membrane parameters that may impinge on the charge conduction using a method independent of the electrical performance. One parameter crucial to the movement of an ion or ion complex would be the viscosity. Plasticized polymer membranes are descendants of the "liquid membranes" and are frequently visualized as a liquid supported by an inert polymer matrix. The plasticized membrane is not obviously viscous, the microviscosity is not easily measured, and the relationship between microviscosity and ion conduction has not been clearly established. It is the purpose of this study to demonstrate a method for measuring the membrane microviscosity and show that it is related to ion movement, as measured by ac impedance, and that it can be used to gain greater insight into the mechanism of charge conduction.

Neutral-carrier ion-selective electrodes use plasticized polymer membranes as the ion-selective element. The hydrophobic membrane blocks the movement of ions but can be made electrically conductive by doping it with a mobile ion carrier. These neutral carriers, so named because they are themselves electrically neutral, such as valinomycin or corwn ether, can facilitate transport of ions from an aqueous phase into the organic membrane thus imparting permselectivity to the membrane. Valinomycin is a cyclododecadepsipeptide antibiotic which forms a cage

† Current address: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180

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structure capable of complexing K^+ and transporting it into a nonpolar solvent.[1] The mobility of the charge carrier is an important variable in the performance of neutral-carrier ion-selective electrodes.

The membrane has been described as a viscous liquid[2-4] containing three distinct structural regions: plasticized polymer, plasticizer, and hydrophilic pockets, possibly water clusters.[5] The measurement of electrical resistance through the bulk of the membrane has allowed the estimation of the ion carrier mobility, its diffusion coefficient and even membrane "viscosity". But interpretation of these terms is difficult due to the almost certain molecular heterogeneity of the membrane; some fraction of the carriers may be trapped in the PVC network, while others are free to move in the plasticizer pools. There is also question about the identity and function of counter ions. The membrane must maintain electrical neutrality, but is this done through fixed or mobile anionic sites? Or are undissociated ions pairs formed in the membrane, and if so, how do the counterions affect conductivity, selectivity, and overall electrode performance? In this work, we propose the use of fluorescence anisotropy for studying membrane microviscosity and its importance to molecular mobility in the membrane and charge conduction.

Steady-state fluorescence anisotropy has been applied extensively to measure fluidity of biological membranes[6] by monitoring the rotational rate of a small fluorescent molecule, such as 1,6-diphenyl-1,3,5-hexatriene (DPH), inserted in the membrane. The Brownian (rotational) movement of the fluorescent molecule is monitored by observing the polarization state of photoemission upon photoexcitation by plane-polarized light. Molecular tumbling will result in randomization of the molecular orientation and, if it occurs during the excited state lifetime, will be observed as a depolarization of the emitted light. The anisotropy of the emitted light will be a sensitive probe of the rotational rate of the molecule and can give information about the mobility of the molecule and the fluidity of the environment, as expressed by the Perrin–Weber[7] equation, (eq 1), where r is the measured anisotropy and r_0 is the anisotropy in the absence of rotation. R is the gas constant, T is the temperature, τ_f is the fluorophore excited-state lifetime, η' is the local viscosity or "microviscosity", and V is the molecular volume of the probe.

$$\frac{1}{r} = \frac{1}{r_0}\left(1 + \frac{RT\tau_f}{\eta' V}\right) \tag{1}$$

Theory

The electrical resistance of the membrane is directly proportional to the viscosity experienced by the charge carrier. We can see this relationship by considering the electrical current through the membrane as ions accelerated through a viscous solvent by an electric field:

speed of a particle = accelerating force/frictional drag

The friction coefficient, f, of a spherical particle of radius a_j in a solvent of viscosity η is given by the Stokes' relation:

$$f = 6\pi a_j \eta \tag{2}$$

Normally, the viscosity used is of the bulk solution, but in this application we will be measuring the microviscosity, η'. The spherical particle is the ion or ion-containing species responsible for carrying the current, valinomycin in this study. The accelerating force acting on a charged particle in an electric field is given by

$$F = z_j e E \tag{3}$$

where $z_j e$ is the charge on the ion and E is the electric field. The electric field results from two electrodes separated a distance l with potential difference ΔE, such that $E = \Delta E/l$. So the speed of a charged particle in an electric fields is given by

$$v_j = \frac{z_j e \Delta E/l}{6\pi\eta' a_j} \tag{4}$$

The electric current is a measure of the amount of charge passing a given point in a given time and can be calculated from the velocity of the charged particles, the charge on each particle, $z_j e$, the concentration of particles, $c_j N$, and the area, A, through which current flow:

$$I_j = v_j z_j e c_j N A \tag{5}$$

Substitution of ion velocity from eq 4 gives the current due to an ion moving in a solvent of viscosity η' accelerated by a potential ΔE:

$$I_j = \frac{z_j^2 e^2 c_j N A \Delta E/l}{6\pi\eta' a_j} \tag{6}$$

Finally, we can get to the electrical resistance as the ratio of the potential to the resulting current, as given by Ohm's law, $\Delta E = IR$:

$$R = 6\pi\eta' a_j l/z_j^2 e^2 c_j N A \tag{7}$$

The resistance is expected to be directly proportional to the viscosity. Fluorescence anisotropy can give us the membrane microviscosity and allow us to monitor other terms, such as the concentration of charge carriers or possibly the carrier size and maybe the diffusion coefficient. If we plot membrane resistance as measured by ac impedance against the membrane viscosity calculated from the measured fluorescence anisotropy for a series of membranes with varying viscosities, we should have a straight line with slope given by the terms in the equation.

The presence of multiple structural regions in the membrane demand care when interpreting steady-state fluorescence anisotropy strictly in terms of a viscosity effect. As pointed out by Lakowicz et al.,[8] the steady-state fluorescence anisotropy will give only an average over all the microenvironments and cannot by itself distinguish between slow rotation due to viscous drag and hindered rotation due to steric barriers. The plasticized membrane surely presents multiple environments to the fluorescent probe, with various degrees of rotational hindrance, and the measured anisotropy represents an average over all states. The interpretation of the anisotropy in the membrane must be in terms of microviscosity and steric hindrance. This same caution must be exercised when interpreting the electrical studies involving the neutral carrier membrane. It may be possible to separate the observation of anisotropy, into microviscosity and restricted rotation, by observing dependence of the anisot-

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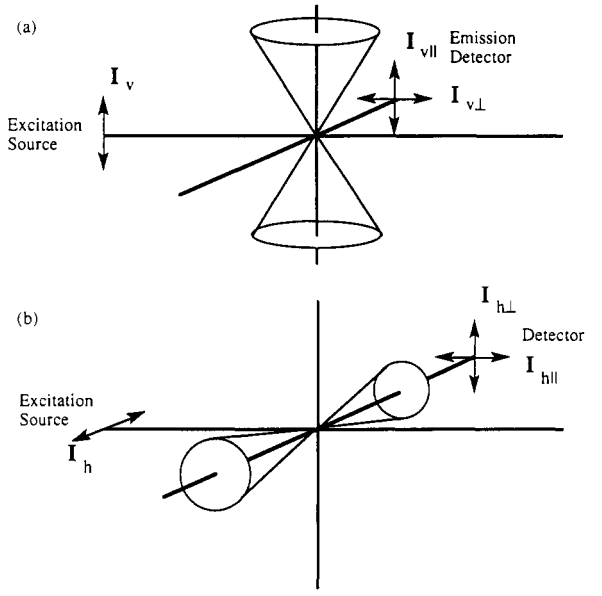

Figure 1. Measurement of steady-state fluorescence anisotropy: (a) vertically polarized excitation, (b) horizontally polarized excitation.

ropy on plasticizer viscosity and membrane temperature. The experiments in this paper have been structured to allow interpretation in terms of viscosity effects.

Experimental Section

The chemicals used for membrane fabrication were purchased from Aldrich and used as received except the tetrahydrofuran which was distilled over potassium to remove water. The membranes were assembled by dissolving poly(vinyl chloride) (PVC, very high molecular weight), plasticizer (dibutyl sebacate (DBS), diethyl sebacate, dimethyl sebacate, or bis(2-ethylhexyl) sebacate), and either the fluorescence probe, 1,6-diphenyl-1,3,5-hexatriene (DPH), or the ion-carrier valinomycin, in tetrahydrofuran (THF). The membrane solution was poured in a circular mold and the THF allowed to evaporate.

Steady-state fluorescence anisotropy was measured on a Perkin-Elmer LS-5 luminescence spectrometer fitted with the polarization accessory consisting of rotatable polarizers in the emission and excitation beams. Excitation was at 355 nm, and the luminescence was observed at 430 nm with both the excitation and emission monochrometers set to 5-nm bandpass. Temperature control was achieved by circulating water from an external bath through the cell holder.

The anisotropy measurement consists of exciting the sample with vertically polarized light and recording the magnitude of the luminescence detected either parallel or perpendicular to the polarization of the excitation beam, $I_{V\|}$ and $I_{V\perp}$ respectively, Figure 1a. The difference, $I_{V\|} - I_{V\perp}$ is a measure of the amount of rotation during the excited-state lifetime. This difference is divided by the total luminescence, $I_{V\|} + 2*I_{V\perp}$, to give the anisotropy. The measurement is complicated by optical artifacts in the form of unequal transmission of the vertical and horizontal polarized light by the emission optics. This is corrected using the horizontal orientation of the excitation polarizer, Figure 1b. In this case the luminescence can reach the emission optics only through 90° rotation of the molecule in either the vertical or horizontal direction yielding $I_{h\perp}$ and $I_{h\|}$, respectively. In an isotropic medium equal numbers of molecules should reach both orientations and the respective luminescent intensities should be equal, $I_{h\perp} = I_{h\|}$. This can be exploited to create a correction factor, G, as defined in eq 8. The correction factor was close to 1 and dependent on the emission wavelength monitored but independent of sample viscosity, as expected:

$$r = \frac{I_{v\|} - I_{V\perp}*G}{I_{v\|} + 2*I_{V\perp}*G} \qquad (8)$$

$$G = I_{h\perp}/I_{h\|}$$

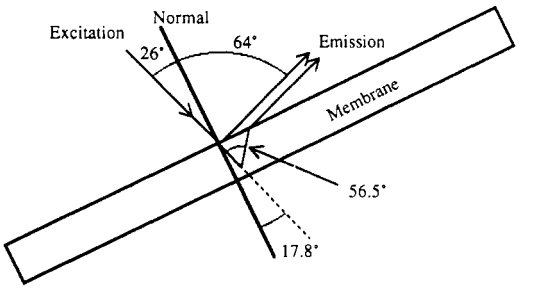

Figure 2. Incident light geometry for the front surface accessory.

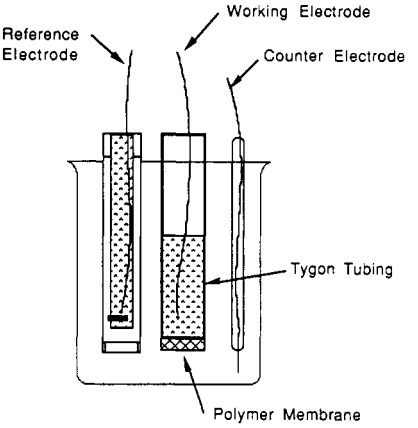

Figure 3. Electrode construction and configuration for measurement of ac impedance.

For measurement of fluorescence anisotropy from the membrane, the Perkin-Elmer polarization accessory was mounted onto the front surface accessory. The excitation beam struck the membrane approximately 26° from the normal with the emission still monitored 90° from the excitation; see Figure 2. Again the anisotropy was calculated from the measured luminescence at each polarizer orientation using eq 8. For these membranes studies, though, we have used the correction factor, G, measured with the solutions as explained in the results section. A special membrane holder was constructed to enable temperature control with the circulating bath.

The ac impedance measurements were made with an EG&G Princeton Applied Research Model 362 scanning potentiostat/galvanostat operating in the galvanostatic mode. A sinusoidal waveform, generated by the lock-in amplifier, was applied, and the in-phase and out-of-phase ac components of the resulting driving potential were detected and measured with a Stanford Research Systems SR530 lock-in amplifier. The amplifier was controlled by a Textronix graphics computer through an IEEE interface. The software scanned frequency from 5 Hz to 100 kHz and collected data for each point in the run. The data were then transferred to an Apple Macintosh computer for analysis and display. The electrode arrangement was as follows: A $^5/_{16}$-in.-diameter disk was cut from the doped PVC membrane and attached to one end of a 1-in. piece of $^5/_{16}$-in.-o.d. Tygon tubing using a small amount of tetrahydrofuran to soften the tubing. The tube was filled with 0.01 M KCl and a chlorided silver wire was inserted into the open end; see Figure 3. The silver wire was connected as the "working" electrode in a three-electrode configuration with a double junction reference electrode in the external solution, also 0.01 M KCl, along with a platinum wire "counter" electrode. Temperature was controlled through a jacketed sample beaker connected to a circulating bath.

Results

Observation of DPH in Membrane. The fluorescence emission spectra of DPH was observed in all samples; unlabeled membranes gave very low background luminescence. The magnitude of the anisotropy was independent of the DPH concentration while the standard deviation of the measurement decreased with increasing

Table I

sebacate ester	viscosity (20 °C), P	anisotropy (20 °C) solution	anisotropy (20 °C) 30% PVC membrane
dimethyl	0.04 (30 °C)	0.015 (30 °C)	0.14 (20 °C)
diethyl	0.057	0.019	0.094
dibutyl	0.075	0.028	0.11
bis(2-ethylhexyl)	0.212	0.047	0.18

concentration. The DPH concentration used in subsequent studies was chosen to minimize signal variance while remaining in the linear region of a total luminescence vs concentration plot.

Sensitivity of Anisotropy to Viscosity. To test the sensitivity of fluorescence anisotropy to membrane microviscosity, membranes were made with plasticizers of varying viscosities. The viscosity of the sebacate esters, determined with an Ostwald viscosimeter referenced to water, is listed in Table I with the measured anisotropy from the liquids and corresponding membranes. The anisotropy is clearly sensitive to the viscosity of the plasticizer both in the liquid solutions and in the membranes.

Calibration of Anisotropy. The Perrin–Weber equation would allow us to calculate the microviscosity directly from the measured anisotropy if we had accurate values for all the terms in the equation. However, at this time we have only estimates of the fluorescent state lifetime and the molecular volume of the DPH and so have calibrated the observed anisotropy using independently measured viscosity. We have chosen as a reference the liquid plasticizers, for which we can determine the bulk viscosity and assume equivalence of microviscosity.

The calibration consisted of measuring the bulk viscosity, η, of various plasticizers with an Ostwald viscosimeter as well as the fluorescence anisotropy in the solutions. A plot of $1/r$ versus T/η yielded a straight line, Figure 4, in accord with the Perrin–Weber equation, eq 1. The linearity of the data for each solution suggests that τ_f does not vary with temperature within our range in this environment. While the various plasticizers have all fallen on the same line, within experimental error, we have used *only* the DBS solutions as the reference for the membranes plasticized with DBS.

The slope of the line should be given by $R\tau_f/r_0V$ with intercept of $1/r_0$ at $T/\eta = 0$. We can estimate these terms to compare with our experimental values as a check of our results. The theoretical maximum value of r_0 is 0.4 for the case of parallel excitation and emission dipoles[7,9] and has been experimentally determined by Lackowitz et al. to be 0.39 for DPH.[8] In the same study, τ_f for DPH was found to range from 9.9 ns in mineral oil to 4.5 ns in ethylene glycol with little variation of the lifetime with temperature for the mineral oil between −20 and 60 °C, but a temperature dependence in the ethylene glycol. For a rough estimate for the constant term in the Perrin–Weber equation, we have assumed the sebacate esters to be similar to the mineral oil and have assigned a lifetime of 9.9 ns. The molecular volume, V, calculated from molecular dimensions derived from a computer-generated model, is about 400 Å^3. Combining these estimates gives a theoretical slope of 0.009 ± 0.001 P/K in good agreement with the experimental data, 0.010 P/K. The extrapolated intercept, 2.0, is within experimental error of the reported $1/r_0$.

As the first reported measurement of steady-state fluorescence anisotropy from a planar surface, we attempted to demonstrate the technique on a system of known viscosity or at least of expected anisotropy. A membrane of unplasticized PVC was chosen because the DPH would be expected to be held rigidly and should give $r = r_0 = 0.39$. Such a membrane was constructed (100% PVC + DPH) and gave a measured anisotropy of 0.5 when calculated as described above. This value is high, but of more concern is that the optical correction factor, G, was found to be 0.63 as opposed to 1.06 for the solutions. We suspected that the polarization state of the excitation beam was altered by the angle of incidence on the membrane.

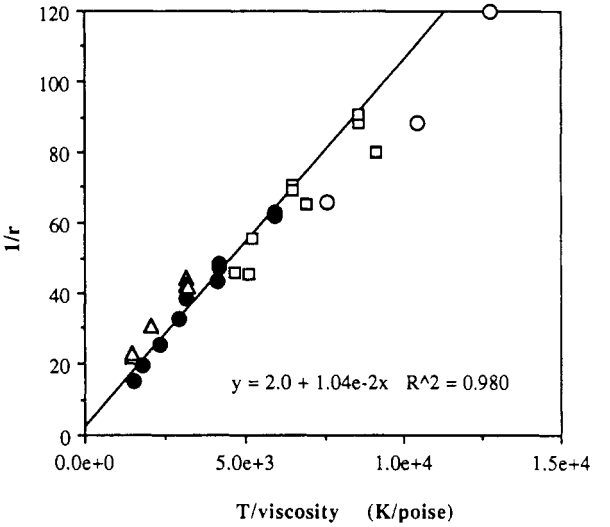

Figure 4. Viscosity calibration with sebacate ester solutions; dibutyl sebacate (●), bis(2-ethylhexyl) sebacate (Δ), diethyl sebacate (□), and dimethyl sebacate (○). The reference line is for dibutyl sebacate data only.

Geometric consideration indicates that $I_{h\parallel}$ and $I_{h\perp}$ no longer arise from equal fluorophore rotation because of the angle of incidence of the excitation beam on the front surface accessory. The excitation beam strikes the film 26° from the normal, Figure 2. If the refractive index of the film is assumed to be 1.4 (that of the plasticizer), the angle of the refracted beams is 17.8° from the normal. Thus for a molecule to absorb light that is horizontally polarized (in the optical plane defined by the excitation and emission beams) and then emit light that can be detected with a horizontally oriented detector, it must rotate 17.8° − (−38.7°) = 56.5° in the optical plane. To produce vertically oriented luminescence, the excited molecule must rotate 90° out of the optical plane. Assuming isotropic rotation, it would be expected that the luminescence is inversely proportional to the angle of rotation and thus the ratio of intensities, $I_\perp/I_\parallel$, would be 0.628, as was observed; therefore, G is no longer an optical correction factor but dependent on the angle of the membrane. For the membrane calculations, we have used the correction factor determined with solutions since G is a function of the intrumental configuration of the emission optics and should be valid with any sample. Using this value, the anisotropy for the 100% PVC membrane was found to be 0.33, indicating some depolarization at the membrane surface or possibly residual molecular motion in this matrix.

While liquid solutions were used for the calibration, the samples of interest are membranes, so it is important to discuss the possible limitations of this procedure. The introduction of PVC may change the magnitude of τ_f as well as the temperature dependence. The introduction of PVC increases the dielectric constant from approximately 4 in dioctyl sebacate to 10 in the plasticized membrane.[5]

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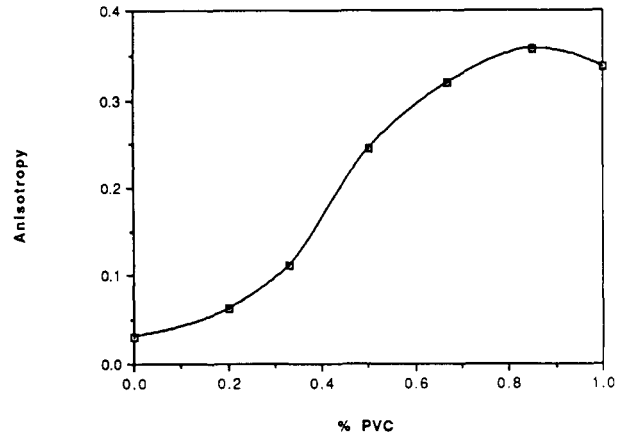

Figure 5. Anisotropy as a function of %PVC in a series of membranes plasticized with dibutyl sebacate.

This is still much lower than the 37.7 of ethylene glycol. Although expected to have little effect on the fluorescence lifetime, a cautious approach would advise maintenance of a constant PVC presence in any series of experiments. The introduction of a temperature dependence into the lifetime is of more concern due to our use of temperature to control viscosity both in the solutions and the membranes. The linear nature of the data for each solution ($R\tau_f/r_0V$ is constant) supports the assumption of constant τ_f over the tested temperature range for the solutions. A 100% PVC membrane doped with DPH showed very little temperature dependence, supporting the assumption of constant τ_f in the presence of PVC. As a final point, Hare and Lussan[10] have demonstrated the dependence of the calibration on the specific reference material chosen; that is, various aliphatic solvents with constant macroscopic viscosity give very different anisotropies. The choice of the liquid sebacate esters as a reference should minimize this uncertainty. In the present case liquid dibutyl sebacate will be used as the reference for membranes plasticized with DBS.

Viscosity as a Function of PVC Content. The anisotropy of DPH is also dependent on the PVC content of the medium, as shown in Figure 5. The smooth transition of the anisotropy from liquid ester plasticizer to the unplasticized PVC membrane cannot be interpreted simply as a viscosity effect due to the probable inhomogeneity of the local environment, the DPH may be envisioned as distributed among plasticizer pools of varying sizes with varying rotational restrictions. The transition from low anisotropy to high may be due to the shrinking of these pools. For the low PVC membranes, the anisotropy is sensitive to the plasticizer viscosity.

Membrane Microviscosity and Resistance. It should be possible to calculate the expected membrane resistance given the microviscosity using eq 8, but, once again, we do not have accurate values for all the terms and have chosen to demonstrate experimentally the linear relationship of resistance and microviscosity. Ideally, the resistance and viscosities of several membranes could be measured to generate a plot of R vs η, possibly varying η throuh the use of various plasticizers. In reality we found the resistance to be so dependent on membrane thickness and PVC content that extreme scatter was seen due to the difficulty of controlling these parameters. We have instead used a single membrane to ensure that the terms remain constant and have varied the microviscosity by varying the temperature.

(10) Hare, F.; Lussan, C. *Biochim. Biophys. Acta* 1977, *467*, 262–272.

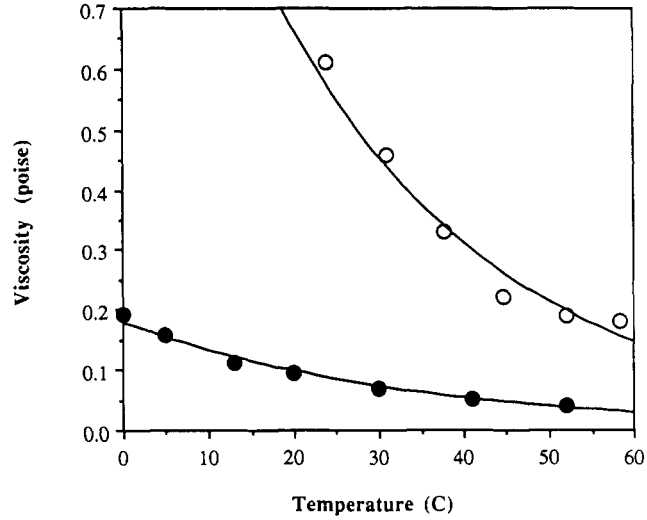

Figure 6. Viscosity as a function of temperature: comparison between dibutyl sebacate: 20% PVC membrane (○) from anisotropy and dibutyl sebacate solution (●) from viscosimeter measurement.

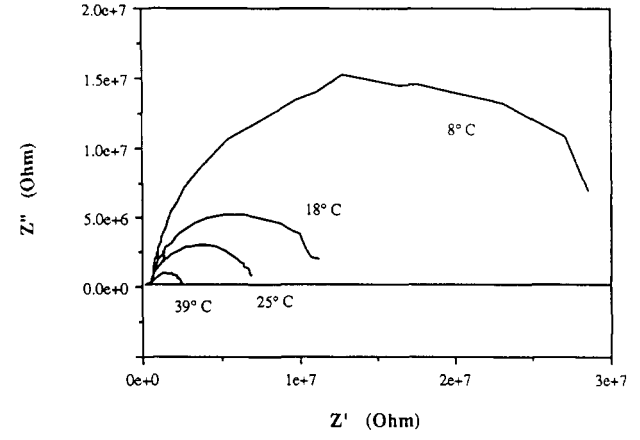

Figure 7. Complex plane impedance plot of 20% PVC:dibutyl sebacate membrane containing 1% valinomycin.

Anisotropy measurements were made from a membrane consisting of 20% w/w DBS, 80% PVC, and DPH mounted on a thermostated front-surface cell for measurement at several temperatures from room temperature up to 58 °C. Membrane microviscosity at each temperature was then calculated from the anisotropy using the viscosity reference curve. Comparison of the membrane microviscosity with the plasticizer bulk viscosity (Figure 6) shows two features of note. First, the strong temperature dependence of the microviscosity suggests the anisotropy is probing the viscosity in the membrane and not simply steric rotational hindrance. However, some steric hindrance may be indicated by the apparent leveling of the microviscosity curve at high temperatures. The apparent membrane microviscosity of a 20% PVC:dibutyl sebacate membrane is 0.6 P. Armstrong and Todd[3] estimated and viscosity in a 33% PVC:bis(2-ethylhexyl) sebacate membrane to be ~600 times that of water or about 6 P. Their estimation was based on bulk resistance measurements and is in line with our number when allowance is made for the higher PVC content and higher viscosity of their plasticizer.

The bulk membrane resistance, measured for a membrane of identical composition except containing the neutral carrier valinomycin instead of the DPH, is strongly temperature dependent, as seen in the superposition of the complex plane ac impedance plots, Figure 7. The data,

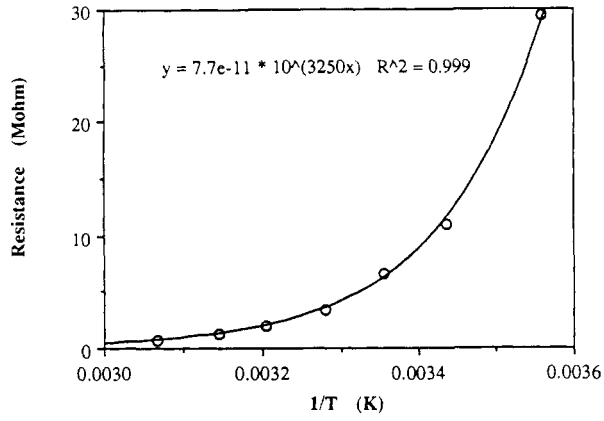

Figure 8. Temperature dependence of bulk membrane resistance for 20% PVC:dibutyl sebacate membrane.

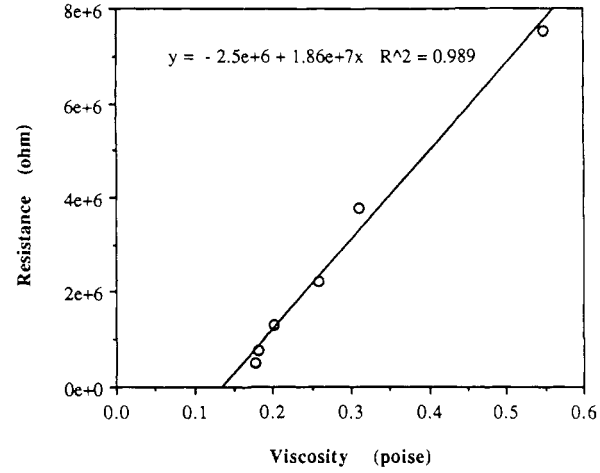

Figure 9. Bulk membrane resistance as a function of microviscosity for a 20% PVC:dibutyl sebacate membrane.

plotted as resistance vs $1/T$, can be fit with an exponential equation (Figure 8) for the purpose of interpolating resistance values at the temperatures for which the anisotropy was measured.

The graph of the microviscosity and resistance is shown in Figure 9. Clearly the data define a linear relationship over the viscosity range tested supporting our derived relationship between resistance and microviscosity. Again, several features of the graph are of interest. The nonzero intercept may be due to the heterogeneity of the microenvironment and the sensitivity of the anisotropy to diphenylhexatriene trapped by the PVC chain, as discussed in conjunction with Figure 6. The measured anisotropy is the weighted average of DPH in each environment, whether trapped by the PVC chain or free in a plasticizer pool. As such the viscosity in the region of the mobile carriers will be overestimated. The current is due to the carriers in the mobile environment and so the measured resistance will reflect the viscosity in these mobile regions. The intercept may provide a means of separating hindered movement from viscosity effects.

The slope of the experimental line can be compared with an estimate for the constant term in eq 7. The values used in the calculation are given in Table II and yield the result

Table II

term	value
a_i ionic radius[a]	0.61 ± 0.09 nm
l distance between electrodes[b]	(3 ± 0.5) × 10^{-4} m
z_i charge on the carrier	1
e elementary charge	1.6 × 10^{-19} C
c_i concentration of charge carriers in the membrane[c]	1.8 ± 0.3 mol/cm^3
N Avogadro's number	6.02 × 10^{23} mol^{-1}
A membrane area through which current flows	(1.2 ± 0.2) × 10^{-5} m^2

[a] Estimated from crystal structure.[1] [b] The ac impedance isolates the resistance of the membrane so the membrane thickness may be appropriate here. [c] As a maximum this would be the concentration of valinomycin. The uncertainty is expressed for total valinomycin.

10 ± 3 × 10^6 Ω/P. The fit line from Figure 9 has a slope of 18.6 × 10^6 Ω/P. The low estimated slope may be attributable to our assumption that the charge carrier concentration is equal to the total valinomycin concentration. This assumption is questionable for two reasons: first, as mentioned above for the DPH, a portion of the valinomycin may be trapped in the PVC structure and not participate in electrical conduction, and second, the membranes were assembled without precharging the valinomycin with K^+ so it is unlikely that all the mobile valinomycin is actively carrying ions. It may be possible to use the ratio of estimated slope to experimental slope, 0.54, as an indicator of the percent of valinomycin actively carrying the current. The other assumed value in the calculated proportionality term, the ionic radius, could also contribute to the observed difference. Armstrong et al.[11] have postulated that the potassium–valinomycin complex is immobile in the membrane and the current is carried by the uncomplexed K^+. Using the smaller ionic radii of the bare potassium ion would decrease the estimated proportionality even more but would also require a new estimate for ionic concentration. Clearly, more work needs to be done to delineate these two parameters.

The correlation of microviscosity, as calculated from the anisotropy of DPH in a membrane, with the resistance, as measured by ac impedance, depends on a correlation of the molecular processes that give rise to the two phenomenon. The microviscosity is measured by the tumbling rate of DPH in the membrane. This argues for the mobility of the molecule, but it is possible that the DPH is locked in plasticizer pools and rotational mobility does not accurately reflect translational mobility. We believe the close approximation of the experimental to the calculated slope supports the conclusion that both ac impedance and fluorescence anisotropy are probing the same processes in the membrane.

Acknowledgment. We gratefully acknowledge the support of Vassar College and the Howard Huges Medical Institute.

Registry No. PVC, 9002-86-2; DBS, 109-43-3; DPH, 1720-32-7; diethyl sebacate, 110-40-7; dimethyl sebacate, 106-79-6; bis(2-ethylhexyl)sebacate, 122-62-3; valinomycin, 2001-95-8.

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