where

$$y = r/R_1$$

Before evaluating the integral in eq 4A, we need to rewrite the velocity expression in terms of the average velocity rather than u_1:

$$u_m = \frac{2u_1}{R_1^2}\int_0^{R_1}\{1 + q[1 - (r/R_1)^2]\}r\,dr \qquad (5A)$$

where

$$q = \Lambda C_b E^2 B R_1^2/4k_1T_1^2$$

Integration and rearrangement of eq 5A yields

$$u_m = u_1(2 + q)/2 \qquad (6A)$$

The velocity can be written as

$$u = Fu_m\left[1 + q\left(1 - \frac{r^2}{R_1^2}\right)\right] \qquad (7A)$$

where $F = 2/(2 + q)$.

Substituting eq 7A into eq 4A and integrating gives

$$g(r) - g(0) = \frac{R_1^2u_m}{D}\left(\frac{Fy^2}{4} + \frac{Fqy^2}{4} - \frac{Fqy^4}{16} - \frac{y^2}{4}\right) \qquad (8A)$$

Using the relation

$$\int_0^1 g(y)y\,dy = 0 \qquad (9A)$$

we can solve for $g(0)$:

$$g(0) = \frac{2R_1^2u_m}{D}\left(\frac{1}{16} - \frac{5Fq}{16} - \frac{F}{16}\right) \qquad (10A)$$

Substituting eq 10A into eq 8A yields

$$g(y) = \frac{R_1^2u_m}{D}\left(\frac{Fy^2}{4} + \frac{Fqy^2}{4} - \frac{Fqy^4}{16} - \frac{y^2}{4} - \frac{F}{8} - \frac{5Fq}{48} + \frac{1}{8}\right) \qquad (11A)$$

Once the expression for $g(y)$ is known, we can solve for the integral in eq 3A and obtain the dispersion coefficient K:

$$K = D + \frac{R_1^2u_m^2q^2}{48D(2 + q)^2} \qquad (12A)$$

From the relations $\sigma^2 = 2Kt$ and $H = \sigma^2/L$ the plate height expression shown in eq 13 can be derived. Note that in eq 13, the velocity is indicated by u rather than by u_m.

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RECEIVED for review July 21, 1988. Accepted October 13, 1988.

Photopolymerization of Plasticizer in Ion-Sensitive Membranes on Solid-State Sensors

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Poly(vinyl chloride) membranes containing the K^+ ionophore valinomycin and plasticized with dihexenyl adipate (DHA) can be photopolymerized in the presence of a radical initiator. Photolysis times of 30 min result in ~1.5% reaction of DHA in the presence of O_2 and 8% reaction in its absence, while 90 min is required for 7% reaction with O_2 present. Photolysis for 30 min in air results in a 3- to 5-fold increase in lifetime for membranes coated on solid-state Si sensors, despite the low extent reaction of DHA. The slope of 57.5 mV, and selectivity coefficient for K^+ over Na^+ of 8×10^{-5}, are similar to dioctyl adipate plasticized K^+ membranes. Photolysis for 30 min in the absence of O_2 results in 3-fold increase in lifetime of membrane-coated Si sensors, but the success rate of electrode preparation is only 50%. The probability that polymerization and interfacially induced stresses are a factor in membrane degradation is discussed, as is the relevance to ion-sensitive field effect transistors.

The preparation of integrated potentiometric sensors such as the ion-sensitive field effect transistor (ISFET) often involves coating the device with an organic membrane similar to those used with ion-selective electrodes (ISE) (*1*, *2*). However, the most commonly used poly(vinyl chloride) (PVC) based liquid–liquid junction membranes are not ideally suited to use with solid-state devices, and problems with membrane performance and lifetime arise. Some of the difficulties stem from poor adhesion of the membrane to the device, and mechanical means of improving adhesion have been successful in reducing rapid drift in potential and slow decline in sensitivity (*2–4*). We have reported chemical means of modifying the ion-sensitive membrane to improve adhesion via introduction of about 0.6 wt % OH functionality to the PVC backbone (PVC-OH), and reaction with $SiCl_4$ to form a covalent bond to OH-bearing surfaces (*5–7*). This modification results in 3- to 5-fold enhancement in the lifetime of membrane-coated ISFETs during continuous exposure to aqueous solution. Scanning electron microscopy (SEM) of these devices after long-term exposure showed that the material properties

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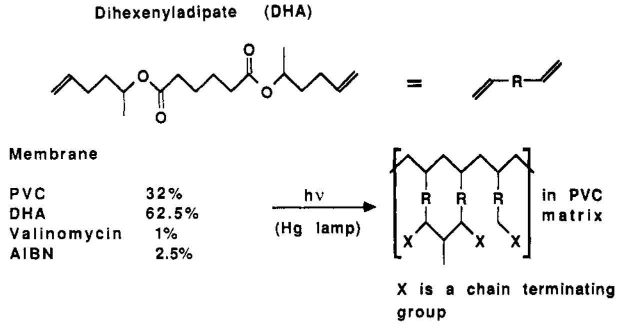
Scheme I



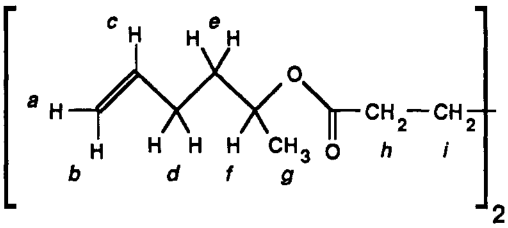
and surface decomposition features observed are significantly different for PVC versus PVC-OH/$SiCl_4$ based matrices. The SEM suggested that cross-linking of PVC-OH through formation of PVC–OSiO–PVC bonds could be an important factor in increasing membrane lifetime (*6*, *7*).

To evaluate the importance of cross-linking membrane components, PVC-based membranes were prepared with a photopolymerizable plasticizer, dihexenyl adipate (DHA). Photoreaction using azo-bis(isobutyronitrile) (AIBN) as a radical initiator, as shown in Scheme I, should lead to oligomerization or polymerization, although the product would probably not be as well defined as indicated in the scheme. The key feature of this approach is that mobility of the plasticizer in the membrane would likely be reduced, and its solubility in water decreased, which are both potentially useful features in membranes coated on integrated devices (*8–10*). At the same time no surface adhesion results from this approach, so the effects of cross-linking can be studied separately. Under certain conditions the proposed scheme was found to increase electrode lifetime just as PVC-OH/$SiCl_4$ modified membranes do; however, extensive DHA reaction appears to be detrimental.

EXPERIMENTAL SECTION

Solvents for liquid chromatography were HPLC grade (Caledon) and used as received. Tetrahydrofuran (THF) and acetonitrile (Reagent Grade, General Intermediates of Canada) were distilled from K and P_2O_5, respectively. Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol–water (mp 102–103 °C). Dioctyl adipate and valinomycin were used as received (Aldrich), as was PVC (Chromatographic Grade, Polysciences) and all other reagents.

5-Hexen-2-ol was prepared by $LiAlH_4$ reduction of 5-hexen-2-one (Aldrich). Under Ar, 3.5 g of $LiAlH_4$ (2-fold excess) in 200 mL of anhydrous ether was cooled in an ice bath in a three-neck, 500-mL round-bottom flask with reflux condenser attached. An addition funnel was used to add 20 mL of 5-hexen-2-one to the magnetically stirred suspension. Thirty minutes after addition of the ketone, 9.3 g of ethyl acetate was added to react with excess $LiAlH_4$. This was followed by 10 mL of 15% aqueous NaOH and 40 mL of H_2O. A Büchner funnel was used to remove the metal salts and the filtrate and precipitate were extracted several times with ether. Flash evaporation of ether on a Rotovap gave 15 mL of a yellow oil. This was distilled under vacuum (aspirator, ~10 Torr) using a short path condenser yielding 10 mL of a colorless liquid boiling between 55 and 56 °C and was not characterized further. Di-5-hexen-2-yl adipate, referred to as dihexenyl adipate (DHA), was prepared via reaction of 5-hexen-2-ol with vacuum distilled adipoyl chloride. With a Schlenk filter, 23.6 g (0.236 mol) of the alcohol was filtered through activated alumina to dry it, and delivered into an Ar flushed three-neck, 250-mL round-bottom flask fitted with a septum, stopcock, and reflux condenser and stoppered with a $CaCl_2$ drying tube. To the flask was added ~50 mL of THF and 18 mL of pyridine (0.223 mol) distilled from BaO under Ar. Adipoyl chloride (20.47 g, 0.112 mol), was added slowly via syringe through the septum into the stirred flask, while cooling the flask in an ice bath. A white precipitate, pyridinium hydrochloride, formed immediately on addition. The mixture was refluxed about 30 min, cooled, washed with 0.1 M HCl, and extracted with ether. The ether extract was washed with H_2O, phosphate buffer at pH 8, and H_2O again, dried over $CaCl_2$, and filtered and the ether was then removed on a Rotovap giving 20.7 g of a colorless oil. The product was vacuum distilled (bp 143–144 °C, ~0.02 Torr) with a short path condenser giving 10 mL of the major fraction. Microanalysis gave 69.9% C and 9.60% H (theoretical C, 69.6%; H, 9.74;), HPLC showed the product to be 98% pure, and a spot test with Br_2 indicated presence of olefin functionality. Mass spectroscopy gave a parent ion at 310.22 (calculated 310.43). The infrared spectrum shows the absence of OH functionality, a strong peak at 1725 cm^{-1} due to the ester, and a sharp, moderate strength peak at 1640 cm^{-1} consistent with the olefinic functionality. The 400-MHz proton NMR spectrum indicates the compound is racemic, due to the chirality of the β carbon in the 5-hexen-2-yl moiety. The spectral assignments are as follows: a, 4.95 (dd, $J_{ab} = 1$ Hz, $J_{ac} = 11$); b, 5.00 (dd, $J_{ba} = 1$, $J_{bc} = 17$); c, 5.78 (ddt, $J_{ca} = 11$, $J_{cb} = 17$, $J_{cd} = 6$); d, 2.06 (m, $J = 7$); e, 1.68 and 1.56 (m); f, 4.91 (dt, $J = 6$); g, 1.2 (d, $J_{gf} = 6$); $h = 2.29$ (t, $J_{hi} = 3$); i, 1.64 (t, $J_{ih} = 3$). The chirality is observed as a splitting of the signal from methylene protons e into two equivalent multiplets.



Membranes were prepared by casting under a THF-saturated atmosphere, from THF solutions of approximately 33% PVC, 65% plasticizer, 1% valinomycin, 0.01% $KB(C_6H_5)_4$, and 0–2.5% azobis(isobutyronitrile) (AIBN) (*11*) (the percentage of PVC and DHA was reduced accordingly). Ion-selective electrodes and membrane-coated Si electrodes were prepared as previously described (*7*, *12*). Membranes were photolyzed with a Hanovia Hg lamp either in air or through a quartz cell that was first evacuated and backfilled with Ar. Selectivity coefficients, k_{ij}, were determined via the Nicolsky equation (*13*), using constant interfering ion while varying the primary ion concentration. While the accuracy of selectivity coefficients is generally recognized to be poor due to their sensitivity to the method of determination, the precision can be high when one method is consistently used for a series of similar electrodes. The precision of $k_{K,Na}$ in these studies is approximately ±5% relative standard deviation. Between trials membrane-coated Si electrodes were stored in 0.1 M NaCl, 10^{-5} M KCl at room temperature. A Fisher Accumet 825 MP meter was used for potential measurements. A Fisher glass electrode was used to determine pH, and a standard calomel electrode (SCE) with a 0.1 M NH_4Cl double junction was used as external reference electrode. A 0.1 M NaCl double junction was used for pH studies. Electrode impedance was determined with an ac impedance measurement system we have recently described (*12*).

Liquid chromatography was performed with a Waters gradient elution HPLC system equipped with an automated gradient controller, two Model 501 pumps operated at 1.5 mL/min total flow, a Lamda Max 481 absorbance detector, operated at 220 nm, a Waters 740 data module, and a 5-μm particle size Novapak C-18 reverse bonded phase column. Samples of membranes for which the initial composition was accurately determined by weight were prepared for injection by sectioning the membrane in half, weighing accurately, adding a known weight of dioctyl adipate (DOA), and dissolving in 1 mL of THF. The PVC was precipitated by addition to 10 mL of acetonitrile (ACN). The solution was filtered and the precipitate rinsed several times with small portions of ACN and diluted to 25 mL in a volumetric flask. The added DOA served as an internal standard and a known amount was also added to the DHA standards prepared in ACN. Due to the large differences in retention characteristics of DHA and DOA, a gradient step was performed 1 min after injection from 80% ACN, 20% H_2O to 100% ACN; however there is a 3.5-min delay before the solvent change reaches the detector due to the volume in the pulse dampeners. The DHA eluted at 2.48 min and DOA eluted at 7.9 min, 1.3 min after the base line had restabilized. The

Table I. Progress of Dihexenyl Adipate Photolysis

sample[a]	% AIBN[b]	photolysis condition[c]	% DHA reacted
DHA	3.5	30 min, air	5.8
	3.6	80 min, air	16
	3.8	30 min, argon	42
membrane	0.25	30 min, air	1.2
	2.5	30 min, air	1.7
	2.5	30 min, argon	8.1
	0.25	90 min, air	4.0
	2.5	90 min, air	7.2

[a] DHA refers to a solution of AIBN in DHA, membrane refers to a complete membrane with PVC, DHA, valinomycin, and AIBN. [b] % by weight of AIBN (azobis(isobutyronitrile)). [c] Photolysis was performed under air or argon after degassing.

Table II. Slope and Selectivity of DHA Plasticized ISEs following Photolysis

photolysis conditions[a]	membrane composition[b]	slope, mV	$k_{K,Na}$[c] $\times 10^5$
no	DHA	57.7	6
no	DHA, 2.5% AIBN	57.5	7
no	DHA, $KBPh_4$, 0.25% AIBN	56.7	5
no	DHA, $KBPh_4$, 2.5% AIBN	57.5	4
no	DHA, $KBPh_4$, 8% AIBN	0	
30 min, air	DHA, 2.5% AIBN	57.4	8
30 min, argon	DHA, 2.5% AIBN	57.3	5
30 min, air	DHA, $KBPh_4$, 0.25% AIBN	57.0	9
30 min, air	DHA, $KBPh_4$, 2.5% AIBN	58.8	8
30 min, air	DHA, $KBPh_4$, 8% AIBN	57.4	8
90 min, air	DHA, $KBPh_4$, 0.25% AIBN	26	13
90 min, air	DHA, 2.5% AIBN	54.7	7
120 min, air	DHA, 2.5% AIBN	53.6	23

[a] No photolysis, or photolysis time with Hg lamp in air, or under argon. [b] Constant PVC and valinomycin quantities present for all membrane compositions. $B(Ph)_4$ is tetraphenylborate. [c] Measured by mixed solution, constant interferent (0.1 M NaCl) method.

calibration curve was prepared by plotting area of DHA peak/area of DOA peak versus mass of DHA/mass of DOA.

A Cambridge S250 scanning electron microscope (SEM) equipped with a Kevex 7000 energy-dispersive X-ray analyzer was used to obtain electron micrographs. A small spot size and low beam current were used to prevent beam damage (*7*). Samples were coated with 200 Å of Au for conductivity. Visual inspection of samples at 200× to 400× with an optical microscope before preparation for SEM showed many of the larger features clearly, indicating they do not arise from sample damage in preparation or due to the electron beam (*7*).

RESULTS AND DISCUSSION

The efficacy of photopolymerization of DHA in PVC-based membranes was examined by using high-performance liquid chromatography (HPLC) analysis to determine the fraction of DHA that remained unreacted. To improve precision, multiple measurements of samples and standards were made and dioctyl adipate was introduced during sample workup as an internal standard. This also served to reduce problems with analyte loss during sample preparation. DHA plasticized membranes with no added AIBN and no photolysis were analyzed by HPLC with a precision and accuracy of ±0.5% compared to the known weight of DHA added to the membrane. Comparison of the data in Table I for polymerization of DHA and AIBN in solution versus in membranes shows that progress of the reaction is much slower in the membrane although it does proceed. A 30-min photolysis of the membrane in air results in about 1.5% reaction, depending on the amount of AIBN added, and this increases with extended photolysis. However, as suggested by the data for photolysis of degassed DHA, the reaction proceeds to a greater extent in the membrane when photolysis is performed under an inert Ar atmosphere. While the reaction products are not eluted from the C_{18} column, the results clearly indicate that DHA undergoes photochemical reaction in the PVC matrix. The lack of eluted products is strong evidence for polymer or oligomer formation, since products such as dihexyl adipate or carboxylate derivatives of the monomer arising from radical reaction with O_2 would be eluted under the conditions used.

The electrochemical characteristics of membranes plasticized with DHA and added AIBN show a variety of effects depending on the conditions of photolysis. Table II shows the slope of response to K^+ and the selectivity coefficient for K^+ over Na^+, $k_{K,Na}$, for membranes mounted in the ISE configuration with solution contacting both membrane faces. The slope and selectivity of unphotolyzed DHA membranes are comparable to those of dioctyl adipate (DOA) plasticized K^+ membranes (*7*). The addition of $KB(C_6H_5)_4$ leads to a slight increase in selectivity (decrease in $k_{K,Na}$). Small amounts of AIBN have little effect; however, when enough is added to cause a precipitate to form in the membrane, response to K^+ is completely lost, as found for a membrane with 8% AIBN. The average selectivity coefficient is 5.5×10^{-5} for unphotolyzed membranes with 2.5% AIBN or less, while the average is increased by about 50% for membranes of various compositions photolyzed 30 min in air. A 30-min photolysis under Ar causes a less significant change in $k_{k,Na}$, giving a value that is 40% less than that found for membranes photolyzed in air. Interestingly, photolysis of the 8% AIBN composition results in disappearance of the precipitate in the membrane and a functional electrode. More extensive photolysis of membranes with 0.25% or 2.5% added AIBN causes a decrease in the slope of response to K^+ and significant increase in $k_{K,Na}$, Table II. There is more scatter in the results at longer photolysis times, suggesting variability in the membranes as a result of extended photoreaction.

Membrane surfaces were examined by SEM following a single calibration of the electrode in solution. Surfaces photolyzed for 0 or 30 min were smooth and featureless at 3000× magnification, corresponding to a resolution of ~0.1 μm or better. However, photolysis for 1 h or more induces many cracks in the surface several hundred micrometers long and about 5 μm wide, with curling of the membrane at the edges of the cracks. Such features could easily lead to shorting of the membrane potential and may arise from structural changes induced by cross-linking (vide infra) or simply from overheating during photolysis. The random pattern of the cracks may account for the greater variability in ISE performance with extended photolysis.

DHA plasticized membranes with added AIBN show an increased response to pH when compared to dioctyl adipate plasticized membranes, as shown in Figure 1. Over the pH range 3–10.5 a DOA plasticized membrane, with no AIBN, shows about a 1-mV change at 10^{-3} M K^+. Whether unphotolyzed, or photolyzed in air for 30 min, membranes prepared with DHA and AIBN show about 6 mV response over the same pH range at 10^{-3} M K^+, with 4.5 mV of this response occurring between pH 8 and 10.5. While this is only a small increase in pH sensitivity, it is noteworthy that when the same membrane composition is photolyzed under Ar only a 1.5-mV change is found over a pH 3–10.5 range. At low pH the electrodes exhibit a negative slope with respect to log [H^+] which is commonly observed for DOA plasticized membranes also (*14*), and this has the peculiar effect of leading to negative values for the selectivity coefficient, $k_{K,H}$. For DHA membranes photolyzed under Ar $k_{K,H}$ is −0.005, while it is somewhat larger in magnitude, −0.015 and −0.016, for the air-photolyzed and unphotolyzed membranes, respectively.

The bulk membrane resistance, R_b, determined from the impedance response of ISE-configured DHA membranes was

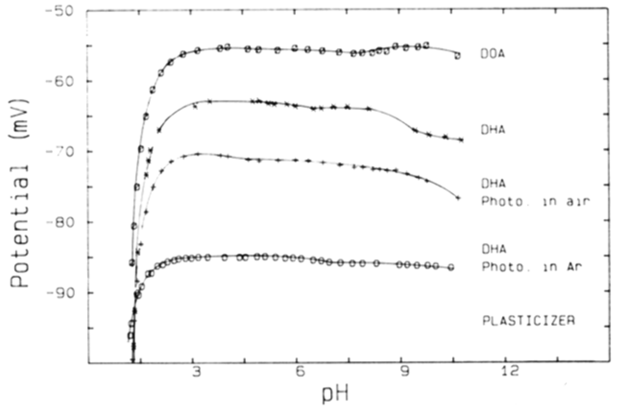


Figure 1. pH response of ion selective electrode configured membranes plasticized with (ϕ) DOA, (*) DHA and 2.5% AIBN; (+) 30 min, air-photolyzed DHA and 2.5% AIBN, and (O) 30-min photolysis under Ar, DHA, and 2.5% AIBN. Measured in 1 mM KCl with 10 mM phosphate as buffer. pH was adjusted with 1 mM KCl, 0.1 M HCl and 1 mM KCl, 0.1 M NaOH.

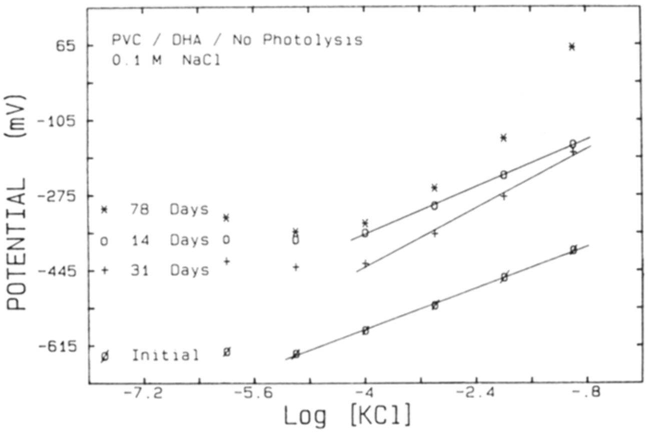


Figure 2. Plot of potential versus log [KCl] in 0.1 M NaCl for DHA and 0.25% AIBN plasticized membrane coated on an n-Si electrode during 78 days of storage in 10^{-5} M KCl, 0.1 M NaCl.

also affected by photolysis, although this parameter does not directly affect K^+ response or selectivity. Photolysis of membranes in air for 30 min decreased R_b by 44% compared to an unphotolyzed membrane for freshly prepared electrodes. When the electrodes were conditioned by soaking in aqueous KCl solution for several days, R_b for the photolyzed membranes was 35% lower than for conditioned, unphotolyzed membranes. For membranes photolyzed 30 min under Ar, a 20% decrease in R_b was observed for freshly prepared electrodes, and only a 10% lower resistance was found after the electrodes were conditioned for several days in aqueous solution.

The effect of photoreaction of DHA on the lifetime of membrane-coated solid-state sensors was examined by using n-Si electrodes coated with 100–200 μm thick layers. We have recently shown that such electrodes respond via a field effect mechanism to concentration changes by a change in open circuit voltage, V_{oc}, relative to a reference electrode (*12*). These n-Si electrodes are also a good model for studying the lifetime of membranes coated on integrated devices on Si, such as the ISFET (*6*, *7*).

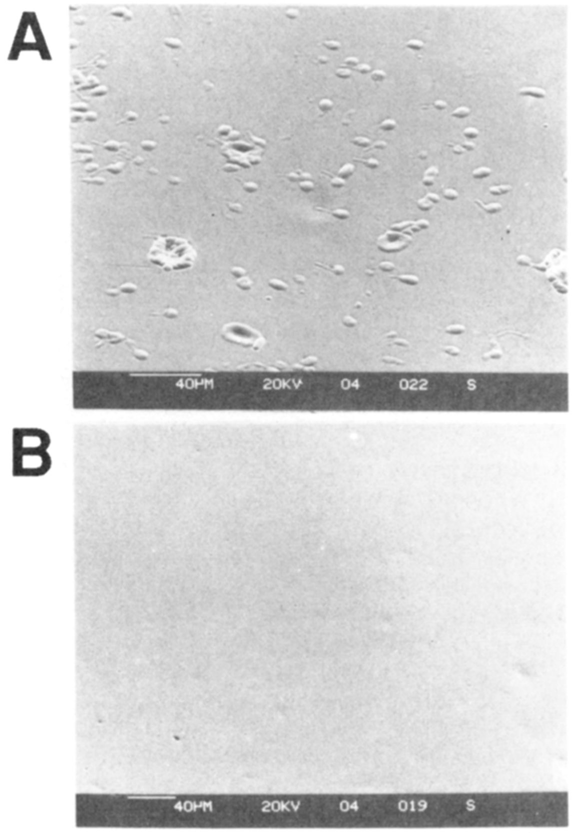


Figure 3. (A) SEM of surface of unphotolyzed DHA electrode in Figure 2, after 78 days of aqueous storage. (B) SEM of surface of photolyzed DHA electrode in Figure 4, after 78 days of aqueous storage. Electrode B had not failed at time of removal from solution.

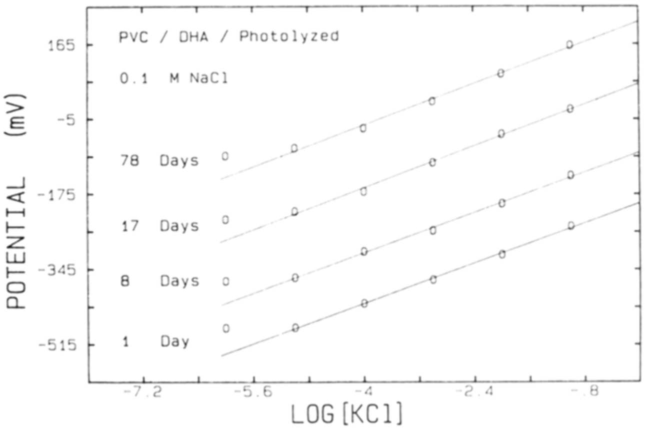


Figure 4. Plot of potential versus log [KCl] in 0.1 M NaCl for DHA and 0.25% AIBN plasticized membrane coated on n-Si electrode after 30 min of photolysis in air, during 78 days of storage in 10^{-5} M KCl, 0.1 M NaCl.

A 3- to 5-fold increase in lifetime is observed when DHA membrane coated n-Si electrodes are photolyzed for 30 min in air, as compared to the same type of electrode with no photolysis. Figure 2 shows the response to K^+ of an unphotolyzed electrode during continuous storage in aqueous solution. After 14 days the limit of detection increased about 10-fold, and after further storage the response became erratic, with increased potential drift, and a nonlinear, apparently super-Nernstian, response to K^+. An electron micrograph of this electrode in Figure 3A shows significant surface deterioration. The large blisters formed on the surface appear to be related to exudation of plasticizer from the membrane, as previously observed for DOA plasticized PVC membranes on solid surfaces (*6*, *7*).

Figure 4 shows that following 30 min of photolysis in air the slope and detection limit of a DHA membrane coated n-Si electrode remains essentially unchanged over 78 days of aqueous storage. There is a slow drift in cell potential, but this is not surprising considering the native oxide layer on the n-Si electrode can be expected to age over this period. Electron micrographs of such electrodes after aqueous storage reveal relatively smooth surfaces with some pitting and possible pinhole formation, as shown in Figure 3B for the electrode of Figure 4. Surfaces photolyzed in air for 30 min show none of the surface damage typically observed for DOA (*6*, *7*) or unphotolyzed DHA plasticized membranes.

For DHA membranes coated on n-Si electrodes and photolyzed 30 min in the absence of O_2, good electrochemical performance can be obtained. However, about 50% of the electrodes prepared under argon fail rapidly during aqueous storage (within 3 days) or never work at all. SEM of the nonfunctional electrodes shows extensive cracking and rippling of the surface on a 10–200 μm scale. In several cases the photolyzed membranes are lifted off the n-Si substrate, or appear to have contracted and separated from the Si–epoxy encapsulant edge. Coated n-Si electrodes photolyzed under Ar that do not fail rapidly show at least a 3-fold extended lifetime compared to unphotolyzed DHA membranes. SEM of these membranes after 25–50 days of aqueous storage shows relatively undamaged surfaces, looking similar to Figure 3B.

While ISEs prepared from membranes photolyzed for 1 h or more in air or Ar still respond to K^+, Table II, membranes coated on n-Si and photolyzed for extended periods generally show much poorer response than the ISEs. Consequently, the lifetime of coated n-Si electrodes subjected to extended photolysis was not examined.

It is perhaps surprising that reaction conditions that lead to only about 1.5% conversion of DHA result in 3- to 5-fold enhancement in lifetime, and the high quality of surfaces found by SEM. It is possible that a thin skin of oligomerized DHA forms at the membrane surface, either through preferential polymerization at the surface where the intensity is greatest, or by adsorption at the surface of oligomers that diffuse to this region. This surface "skin" could reduce the leaching, rippling, and cracking phenomena observed by SEM for DOA (*6*, *7*) and unphotolyzed DHA plasticized membranes. Alternatively, it is possible charged groups introduced in the membrane by photolysis could alter the surface degradation processes. Lindner et al. (*15*) have suggested carboxylate-modified PVC induces different surface properties and that leaching of plasticizer does not occur when these ionizable moieties are present in a membrane. The data we have obtained indicates there is an increase in charge in DHA-plasticized membranes as a result of photolysis in air. There is a much greater drop in bulk membrane resistance for photolysis in air versus Ar, consistent with an increased density of mobile charge sites. One of the species formed by reaction of photogenerated radicals with O_2 would likely be carboxylate derivatives, and these are known to decrease membrane resistance (*12*, *15*). Comparison of the pH response for the two photolysis conditions also suggests there is more acid–base functionality in membranes prepared in air. The data on selectivity coefficients are also consistent with the formation of electroactive products in membranes prepared in air, as $k_{K,Na}$ is about 40% smaller when photolysis is done under Ar. Thus, if the proposal of Lindner et al. is valid, the charged species generated by photolysis in air may play a role in improving the lifetime of plasticized PVC membranes.

There are several effects that may lead to the mixed results obtained with more extensive reaction, perhaps depending on the conditions used. The reduced slopes and increased $k_{K,Na}$ values caused by longer photolysis in air may arise from more extensive formation of the charged species discussed above, to a level sufficient to affect these parameters. However, the rippling and cracking features observed by SEM certainly account for the failure of the membrane-coated n-Si electrodes and may also be responsible for decreased ISE performance. The cracking and flaws observed in the membrane may result from heating during extended photolysis or from stress and strain introduced by DHA polymerization. The same surface features are observed for coated n-Si electrodes photolyzed for 90 min or more in air as for electrodes that have become nonfunctional after 30 min of photolysis in argon. Both of these procedures result in more extensive reaction of DHA, Table I, and the similarity of the degraded surfaces is consistent with degradation induced by stress arising from increased polymerization. It could be argued that the liquidlike state of the plasticized membranes should lead to relief of such stress. However, SEM studies of DOA plasticized PVC membranes that have been deliberately stretched or twisted to introduce stress show substantial surface damage and cracking, and the damaged surfaces do not relax over a period of weeks (*16*).

Senturia has suggested that stress and strain in microfilms on solid-state sensors can have a significant impact on sensor performance (*17*), and the presence of stress or strain in PVC-based membranes coated on sensors is an interesting possibility. It is curious that the electrochemical performance of PVC based membranes mounted in the ISE configuration does not degrade during one or more years of aqueous storage, yet membranes of equivalent thickness coated on solid-state sensors fail over days or weeks and exhibit significant changes in surface morphology (*7*). The covalent bonding of a modified PVC-OH/$SiCl_4$ membrane matrix to the substrate improves the lifetime of membranes on a solid surface but lifetimes equivalent to the ISE configuration have yet to be obtained. Bezegh et al. (*10*) have suggested the shorter lifetime of electrodes with a solid state/membrane interface could result from differences in morphology arising from rapid evaporation of casting solvent from the solid-state sensor. However, we have prepared the solid-state devices under a saturated THF atmosphere and the membranes require about 24 h to dry, which is similar to the drying time of ISE membranes cast in the usual manner (*11*). It seems likely that stress or strain developed in a membrane is less easily relieved when one boundary is fixed by the solid/membrane interface, whereas a symmetric pair of interfaces with solution would allow for relief of the strain by expansion in both directions. The significantly shorter lifetime of DOA plasticized PVC membranes coated on solid-state sensors may be explained as resulting from relief of built-up stress through separation from the substrate and/or splitting of the membrane. Similarly, the poor performance of extensively reacted DHA membranes on n-Si electrodes may be due to stress-induced disruption of the membrane caused by photopolymerization.

CONCLUSION

That the lifetime of membrane-coated solid-state sensors can be increased by modest reaction of photopolymerizable DHA indicates that mechanical means alone may not provide the optimum solution for improvement of solid-state sensor performance. Control and modification of the chemical and physical properties of the membrane to better suit the solid/membrane interface must also be considered. The small changes in selectivity resulting from modification of the membrane are certainly mitigated by the enhanced lifetime when the membrane is coated on a solid substrate. However, more extensive polymerization of the plasticizer may be desirable to further enhance durability by decreasing solubility of the plasticizer (*8*, *9*) or to decrease diffusion coefficients in the membrane (*10*). In this case either chemical or mechanical means of increasing surface adhesion may be necessary to avoid failure of the membrane, due to what appears to be stress-related effects.

ACKNOWLEDGMENT

We thank G. Braybrook for valuable assistance in performing the SEM work and the SEM Lab, Department of Entomology, University of Alberta, for use of the SEM. We also thank O. Hindsgaul for assignment of the NMR spectrum of DHA.

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RECEIVED for review July 25, 1988. Accepted October 28, 1988. We thank the Natural Sciences and Engineering Research Council of Canada for support of this research.

Band Broadening in Electrokinetic Chromatography with Micellar Solutions and Open-Tubular Capillaries

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The band-broadening phenomena that occur in the separation column during electrokinetic chromatography were studied. First in order to let column band broadening dominate, extracolumn effects were studied on the basis of theoretical considerations and experimental data. The limit of injection, which is the length of the tube occupied by a sample solution, was 0.8 mm and that of detection bandwidth along the tube axis was also 0.8 mm. Observed minimum plate height with a 50 μm i.d. open-tubular column was 2 μm under the above conditions. The causes of this band broadening were ascribed to five mechanisms: longitudinal diffusion, sorption–desorption kinetics, intermicelle mass transfer, radial temperature gradient effect on electrophoretic velocity, and electrophoretic dispersion of the micelles (heterogeneity in micelle mobilities). The relative significance of each contribution was estimated by comparing the theoretical consideration with the observed dependence of the plate height on the velocity. The longitudinal diffusion was a dominant factor when the velocity was slow; sorption–desorption kinetics and heterogeneity became significant factors as higher voltages were applied. The intermicelle mass transfer mechanism and temperature gradient effect owing to Joule heating were not important.

Electrokinetic chromatography with micellar solutions (*1*, *2*) is a newly developed chromatographic method that utilizes the technique of free zone electrophoresis in open-tubular capillaries (*3*, *4*). The micelle of an ionic surfactant participates in the distribution of a solute as a moving "stationary" phase and an aqueous solution as the other phase. The micelle and the aqueous phase migrate at different velocities due to the electrokinetic forces, i.e., electrophoretic and electroosmotic effects, which permit chromatographic elution in a time window determined by the velocities of the aqueous phase and the micelle (*2*). That is, the two phases between which the solute is distributed constitute a homogeneous solution, but they move differentially. Although this method obviously belongs to a chromatographic technique, it can be said that this approach has widened the electrophoretic separation technique to include the separation of neutral molecules by an indirect process.

The high efficiencies attainable by capillary zone electrophoresis have been discussed by Mikkers et al. (*3*, *5*), Jorgenson and Lukacs (*4*), and Lauer and McManigill (*6*). The migrational dispersion has been ascribed to differences in electrophoretic mobilities between carrier constituents and sample constituents (*5*), and it has been shown that the asymmetric concentration distribution of the band frequently observed in free zone electrophoresis can be suppressed only by the application of very small amounts of samples (*3*). Jorgenson and Lukacs (*4*) have discussed the possibility that since the electroosmotic flow can approximate to a plug flow, longitudinal molecular diffusion should contribute much to the band broadening in capillary zone electrophorsis, although that contribution is generally negligible in conventional liquid chromatography.

We have reported in a previous paper (*1*) that plate heights of 1.9–3.6 μm were obtained for alkylphenols in electrokinetic chromatography. Similar efficiencies have been observed for (phenylthiohydantoin)amino acids (*7*), chlorinated phenols (*8*), aromatic sulfides (*9*), and nucleosides and oligonucleotides (*10*). In order to attain the maximum performance, we have systematically studied band broadening in this chromatographic method. Sepaniak and Cole (*11*) have recently reported on column efficiency in electrokinetic chromatography and we will compare our results with theirs when it is appropriate.

Instrumental conditions that are necessary for obtaining the chromatogram without any loss of performance characteristics of electrokinetic chromatography are presented first; that is, extracolumn effects such as injection volumes, the cell volume of the detection part of the tube, the time constant of the detector, and the response of the recorder pen are discussed. The observed plate heights under the minimal extracolumn conditions are considered as the results of band

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