indicated.

Registry No. PABA, 150-13-0; carbaryl, 63-25-2; 1-naphthol, 90-15-3.

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Nature of Anionic Sites in Plasticized Poly(vinyl chloride) Membranes

Sir: The working mechanism of neutral-carrier-solvent polymeric membranes is at present still not fully understood. One of the unresolved problems is the origin of the cation permselectivity that is exhibited by commonly used plasticized poly(vinyl chloride) membranes (PVC membranes) (1). This behavior is essential for proper functioning of neutral-carrier membranes, as was already recognized by Perry et al. (2) in 1976. They demonstrated that cellulose acetate membranes loaded with valinomycin only show potassium vs sodium selectivity if cation permselectivity is already present. The generally accepted explanation for this permselectivity is the presence of anionic sites embedded in the membrane. Perry et al. fabricated membranes containing such sites by mixing cellulose acetate with variable amounts of cellulose acetate modified with sulfonic acid groups. However, hitherto the exact nature and origin of anionic sites in PVC, commonly used for the preparation of ion-selective membranes, has not been established.

Thoma et al. (3) proposed a mechanism involving small water clusters, present in the membrane, which contain OH⁻ ions. If this were the case, the bulk conductivity of the membrane would grow with increasing soaking time, a phenomenon that was very recently contradicted by experiments of Horvai et al. (4). Conductivity experiments described in the same paper also exclude the possibility that the anionic sites originate from the tetrahydrofuran (THF) solvent or the plasticizer.

With these results, our efforts were focused on the identification of ionic components in the PVC polymer, using impedance measurements, X-ray fluorescence, secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectroscopy (XPS). We assume that these components may arise from different origins: (1) polymer-bound initiating groups, e.g. $ROSO_3^-$ groups or RSO_3^- groups generated by a metal persulfate anion radical initiator (5); (2) oxidation resulting in RCO_2^- groups (6); (3) remainders of surfactants used during emulsion or suspension polymerization, like alkyl sulfates or phosphates, or dialkyl sulfosuccinates (7). We have used various experimental techniques to disclose the type of the groups acting as anionic sites.

EXPERIMENTAL SECTION

Chemicals. Di-*n*-butyl phthalate (DBP) was purchased from BDH Chemicals, Ltd. THF was obtained from Janssen Chimica and was redistilled prior to use. High molecular weight PVC was obtained from Fluka (referred to as Fluka-PVC) and BASF (referred to as BASF-PVC). Carboxylated PVC (1.4 wt % COOH) was purchased from Janssen Chimica (designated COOH–PVC). All other chemicals used were analytical grade reagents.

Apparatus. Frequency response analysis (FRA measurements) was performed with a Solartron 1170 frequency response analyzer. The applied sinusoidal voltage was 10.0 mV. Pt electrodes with an estimated area of 0.2 cm² were used. It was confirmed that with the concentrations used, and in the frequency range 10^4–1 Hz, the electrode impedance could be neglected relative to the membrane impedance.

XPS measurements were carried out with an ESCALAB MK II (VG, Applications Laboratory) for the survey spectra and a XSAM 800 (Kratos, Applications Laboratory) for the detailed spectra. Note that only after sputtering 900 Å from the surface

Table I. Resistivity and Relative Permittivity of Plasticized Fluka-, BASF-, and COOH-PVC Membranes after 20 Min of Contact with 10^{-3} M KCl Solutions

	$10^8 \rho_b$, Ω cm	ϵ_r
Fluka	21	7
BASF	22	7
COOH	5.5	10

with argon, a sulfur signal was measured.

SIMS measurements were performed with an Ion Microprobe Mass Analyzer (IMMA) (Applied Research Laboratories). The investigated membrane area was 75 × 75 μm^2; N_2^+ ions were applied as primary ions, at 20 keV, 1.5 nA.

X-ray fluorescence spectra were measured with a Philips PW 140 wavelength dispersive spectrometer. A PE crystal was used, and a slow scan was carried out in order to increase the signal to noise ratio.

Procedure. The plasticized PVC membranes were formed by spin-coating PVC–DBP–THF, 1/2/10 (wt), solutions at 1000 rpm on an appropriate substrate. This resulted in the following membrane thicknesses: BASF-PVC, 6 μm; COOH-PVC, 5 μm; Fluka-PVC, 4 μm. Thicknesses were determined by interferometry. Supported by a nylon mesh, the plasticized PVC-membranes were mounted on a plastic cylinder and sealed with a Viton O-ring. The active membrane area was 0.38 cm^2. Samples for XPS and SIMS measurements were cut out of the substrates, and in the case of SIMS measurements a thin gold layer was evaporated on top to avoid too much electrostatic charging of the surface. The charging effect with XPS measurements was excluded by taking the C 1s peak as an internal standard at 285 eV. From the XPS spectrum the ratio of the carbon and chlorine concentration was calculated to vary between C:Cl = 1.9:1 and C:Cl = 2.1:1 (theoretical ratio, 2:1), for the different apparatuses used, which indicates the variation in the sensitivity coefficient with the experimental setup. In the other measurements (detailed XPS spectrum and SIMS spectra) too much uncertainty about the sensitivity factors prevented accurate calculations.

X-ray fluorescence was measured on a pressed pellet made from Fluka-PVC powder without plasticizer. The COOH content of COOH-PVC was determined by potentiometric titration.

RESULTS AND DISCUSSION

Impedance Measurements. We investigated the possibility that carboxyl groups, attached to the PVC, might provide the immobile anionic groups in PVC by comparing the bulk resistivity ρ_b (Ω cm) of COOH-PVC with that of high molecular weight PVC. The bulk resistivity was calculated from impedance plane plots; it is related to the membrane bulk resistance by $\rho_b = (A/d)R_b$, where A is the membrane area (cm^2), d the membrane thickness (cm), and R_b the measured resistance (Ω). In Figure 1 the normalized impedance plane plots are shown for the three polymers. From ω_m (the frequency at which the imaginary part of the impedance reaches its maximum), the relative permittivity ϵ_r can be calculated via $\epsilon_r = 1/\epsilon_0\omega_m\rho_b$. The results are summarized in Table I. From the results in Table I it can be concluded that the bulk resistivity of COOH-PVC is about a factor of 3–4 smaller than that of Fluka- or BASF-PVC. If carboxyl groups in Fluka- or BASF-PVC are responsible for the observed conduction, then the resistivity in COOH-PVC must be lower than that which is actually measured. The difference in resistivity experienced is probably due to the higher relative permittivity, which leads to a higher degree of ionization of present ion pairs. Possibly in COOH-PVC the carboxyl groups contribute to the observed conduction, but in Fluka- and BASF-PVC they certainly are not responsible for the measured resistivity. The gradual increase of ρ_b with time observed with BASF-PVC and to a smaller extent with Fluka-PVC, that was also experienced by Horvai et al. (4), leads to the conclusion that the ionic species are not completely immobile but slowly leach out of the membrane. Therefore, it
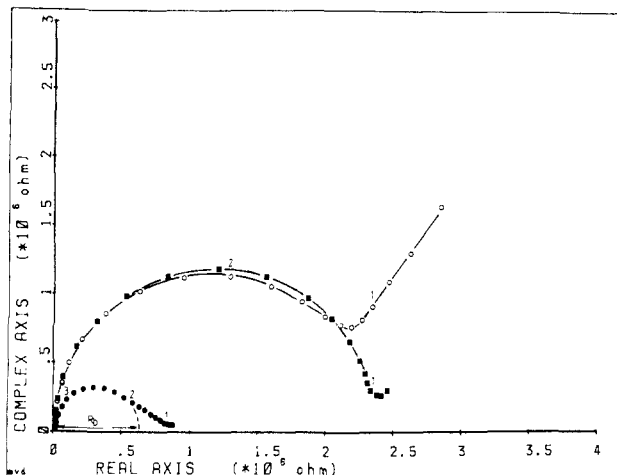

Figure 1. Impedance plane plots of Fluka- (O), BASF- (■), and COOH-PVC (●) in 10^{-3} M KCl after 20 min (normalized to d = 4 μm). The figures on top of the curves indicate the logarithm of the measuring frequency.

is unlikely that these anionic groups are chemically bound to the polymer.

X-ray Fluorescence. We investigated the presence of sulfur- or phosphorus-containing groups in Fluka-PVC with X-ray fluorescence. In the spectrum a small but clear peak was noticeable at θ = 76°, giving an indication for sulfur. Phosphorus was not found by this technique.

SIMS Measurements. We also investigated the Fluka-PVC with SIMS. Both cationic and anionic depth profiles were recorded (Figure 2). From the results shown in Figure 2a it can be concluded that Na^+ and K^+ are initially present in the membrane, probably as counterions for the immobile anions. It should be noted that the amount of Na^+ and K^+ is exaggerated since SIMS is very sensitive to metal cations. In the anion profile (Figure 2b) both S^{2-} and O^{2-} are present in an estimated atomic ratio of $\simeq$ 1:5–10. No phosphorus was detected. Although the sulfur signal was small, it was significantly above the detection limit of the instrument.

XPS Measurements. In order to investigate the chemical state of the apparently present sulfur, we performed XPS measurements. In Figure 3 a survey spectrum of Fluka-PVC is shown. C 1s, Cl 2s, Cl 2p, and O 1s peaks are displayed clearly, and the C:Cl ratio was in agreement with the theoretical value. In the S 2p region a small signal was obtained only with increased sampling time and after sputtering (see Figure 4). The shape of the S 2p peak and its position indicate that the sulfur is present in more than one oxidation state (8). Although some influence of the sputtering procedure on the chemical state of sulfur cannot be excluded, the measurements suggest in our opinion that a mixture of sulfate and sulfonate groups is present in the polymer.

CONCLUSION

From the combined results of FRA, X-ray fluorescence, SIMS, and XPS we conclude that in Fluka-PVC sulfur-containing components are probably present. These components might be sulfate or sulfonate groups and act as the anionic sites. FRA measurements indicate that these sites are presumably present in the form of emulsifier residues, and are not bound to the polymer matrix. The amount of anionic sites appears to be uncontrolled and depends probably on purification methods. In order to avoid this, and to prevent the possibility of leakage toward aqueous solution, it seems favorable to design systems in which anionic groups are solely introduced by attaching them to the polymer. This idea was already suggested and investigated by Cutler et al. (9) in 1977 for surfactant-sensitive membrane electrodes and proved to
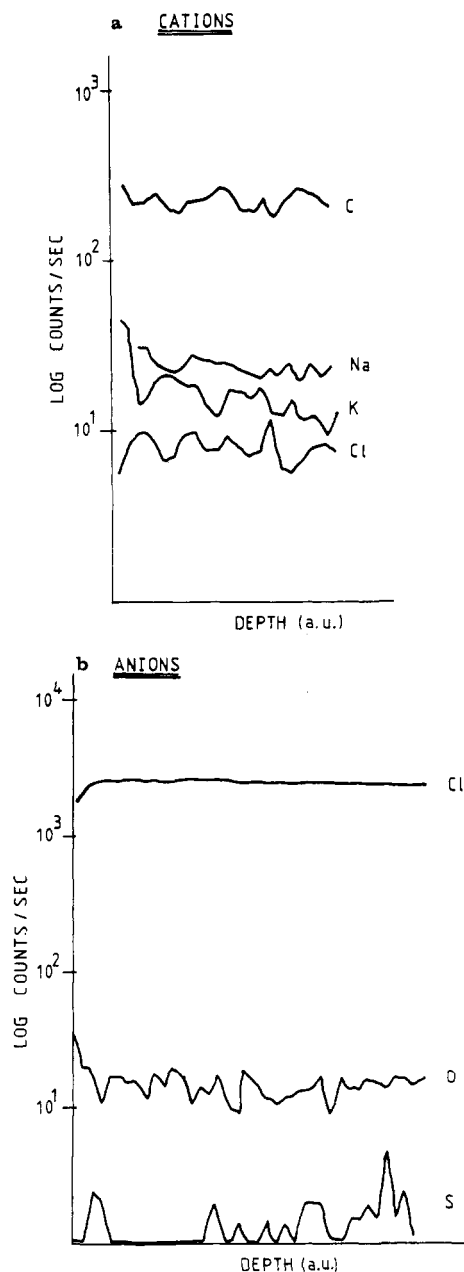
Figure 4. Detailed XPS spectrum of S 2p region (acquisition time 20 min; measured after sputtering 900 Å).

Figure 2. (a) Cation depth profile of Fluka-PVC. (b) Anion depth profile of Fluka-PVC.
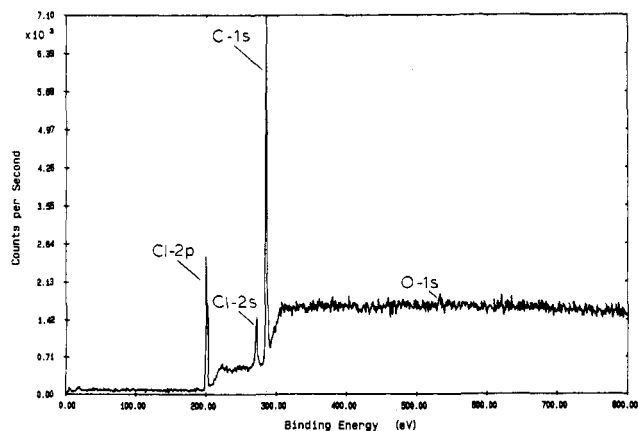

Figure 3. XPS survey spectrum of Fluka-PVC.

be rather successful. However, the role of water in the ion-sensing mechanism should not be underestimated, for example, its influence on the relative permittivity or on the ionic dis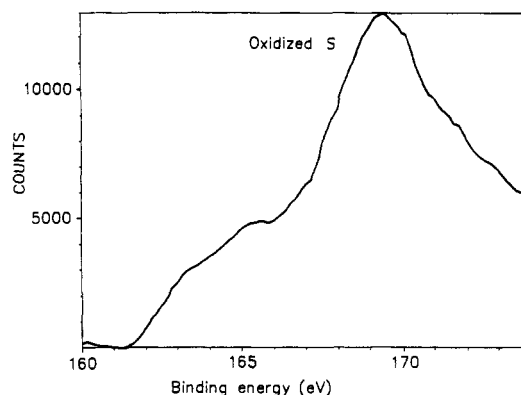sociation. The relatively large water uptake observed with plasticized PVC membranes (4) could well be caused by emulsifier residues. Their well-known ability to form reversed micelles (10) may contribute to the formation and stabilization of the water clusters (11). Further investigations are necessary to clarify whether or not emulsifiers are essential membrane components for proper functioning of ion-selective electrodes.

ACKNOWLEDGMENT

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