Low Frequency Dielectric Dispersion of Microporous Membranes in Electrolyte Solution

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The electrical properties of microporous membranes in 1 mM KCl solution have been investigated in the frequency range 1 mHz to 1 kHz, using a four-electrode measuring cell. An alpha-dispersion centred around 0.1 Hz was detected and this was assumed to be caused by counterion relaxation effects in the pores of the membrane. Schwarz theory was used to provide a rough estimate on the results to be expected from the measurements. This study is part of a project of which the objective is to reveal the contribution from the electrical properties of the sweat ducts to the total electrical properties of the epidermal stratum corneum. Although the phase angles measured on the membranes were small (<2.9°), more data are needed before any conclusions regarding human skin can be drawn.

Key Words: membranes; pores; dielectric dispersion; counterions; stratum corneum.

I. INTRODUCTION

The variation of relative permittivity with frequency in biological materials is well documented but not completely understood. The value of ε decreases with increasing frequency and is commonly in excess of several hundred thousand at subaudio frequencies. Yamamoto and Yamamoto (1) report a relative permittivity for the stratum corneum of about 2 × 10³ at 100 Hz and 1 × 10³ at 1 Hz. This is known as the alpha dispersion and is probably caused by counterion polarization effects (2). Yamamoto and Yamamoto (1) attribute this phenomenon to the keratin layers.

This is not the only possible explanation, however, and we find it necessary to investigate whether this low frequency permittivity increment also could be a sweat duct effect.

The alpha dispersion is associated with a net displacement of counterion charge relative to the center of symmetry of the particles under the influence of an external electric field, resulting in a large field-induced dipole (3, 4) (Fig. 1a).

This phenomenon is also likely to occur in charged membranes with cylindrical pores (Fig. 1b). As on the particles, the counterions will be subject to both the applied electric field and electrostatic attraction to discrete charges in the solid surface. The resulting diffusion process should give a capacitive admittance component when measuring on charged microporous membranes in a four-electrode cell. This paper focuses on the detection of such lateral double layer polarization in microporous polycarbonate membranes, whereas the possible correlation to human sweat ducts is a topic for further investigation.

II. THEORY

Takashima (5) deduces the expression for the dielectric increment of a suspension of long cylinders by transforming the relations for ellipsoids from rectangular to cylindrical coordinates (There is a minor misprint in this formula in Takashima’s book.),

$$\Delta \varepsilon = \frac{e^2 \sigma_0 a^2}{b k T} \frac{9p}{2(1+p)^2} \frac{1}{1 + j \omega \tau} \quad \text{if } a \gg b, \quad [1]$$

where

- ε = elementary charge
- σ₀ = surface density of charged groups
- a = cylinder length
- b = cylinder radius
- T = temperature
- p = volume fraction of cylinders
- j = the imaginary unit
- ω = applied angular frequency
- k = Boltzmann constant
- τ = relaxation time

The relaxation time τ is given by

$$\tau = \frac{(a^2 + b^2)e}{2ukT} \approx \frac{a^2e}{2ukT}. \quad [2]$$

The counterion mobility u should be smaller than the mobility u₀ in free solution, and the following relation is given by Schwarz (6):

$$u = u_0 e^{-a/kT}. \quad [3]$$

The activation energy α is of electrostatic origin. Provided that the minimum distance between the counterion and the
A constant current circuit was achieved by comparing the output to a lock-in amplifier as in Fig. 2, where a current of 100 nA rms was used in measurements. The current-electrodes in this setup were 1 mm stainless steel wire. The wires were placed in the total circumference of the cell to obtain a large surface area and hence reduce the polarization impedance. They were furthermore withdrawn 2 mm from the measuring area to reduce their influence on the measured values, and the compartments were made slightly wider than the wires to allow a large part of the wire to be in contact with the electrolyte.

The membranes used were 6-μm-thick Nuclepore polycarbonate membranes. These membranes have $3 \times 10^8$ pores/cm$^2$ with a pore diameter of 100 nm. The pores are cylindrical with a length equal to the membrane thickness. To increase the impedance of the porous membranes, a thin layer of Vaseline was applied on both sides of the membrane, leaving only a small open area of about 1 mm$^2$. The setup was calibrated at each frequency with the measuring cell without membrane. Measurements were also carried out on polycarbonate film without pores and no dielectric dispersion was found in the 1 mHz to 1 kHz range in these measurements.

The lock-in amplifier was a Stanford Research Model 850 which is a digital lock-in amplifier with a relative phase error of 0.001°. The errors in the measured voltages or currents are typically 1% of full scale.

The ζ-potential of the same Nuclepore polycarbonate membranes with geometrical capillaries were determined at the University of Lappeenranta, Finland, using streaming potential measurements (8). The ζ-potential was found to be $-17.37$ mV in a 1 mM KCl solution at pH 5.5. The same KCl-solution was used in the four-electrode measurements.

### IV. Calculations

The dielectric increment caused by these membranes in the KCl solution can be calculated using the theory in the previous section. The activation energy $a$ is $5.9 \times 10^{-21}$ J when $e_a = 78$ and $\delta = 0.5$ nm. The distance between counterion and surface charge is difficult to predict, however, but it is probably in the range of a few tenths of a nanometer.

Furthermore, distances of less than about 0.6 nm will yield an effective relative permittivity that is lower than the value of pure water. The lower limit of $e_a$ should be about 4.7 according to Pethig (4). The values for $\delta$ and $e_a$ are therefore used as adjustable parameters later in this paper to see whether the calculated dielectric dispersion can be made to fit the measured data with reasonable values for these parameters.

The surface mobility of counterions can be calculated using Eq. [3], with the mobility of the $K^+$ counterions in free solution $u_0 = 7.6 \times 10^{-5}$ m/Vs (9). The relaxation time $\tau$ is calculated using $a = 6 \times 10^{-6}$ m in Eq. (2).

Equation [1] includes the surface density of charged groups $\sigma_0$. This quantity can be calculated from the zeta-potential $\zeta$. First, however, the product $\kappa b$ (the ratio between the cylinder radius and the thickness of the double layer) must be calculated, in order to decide whether flat or spherical double layer approximation should be used. $\kappa$ is given as

$$\kappa = e^{\frac{2n}{\varepsilon_0\varepsilon_0 kT}},$$

where $z$ is the valence of the counterions. If $\kappa b > 1$ then flat double layer approximation should be used. Because of the low zeta potential we may furthermore use Debye–Hückel approximation (10), which gives for the surface density of charged groups,

$$\sigma_0 = \frac{\Psi_0 e \varepsilon_0 \varepsilon_0 \kappa}{e}.$$
where $\Psi_0$ is the surface potential which can be assumed to be equal to the zeta potential (probably slightly larger, however).

V. RESULTS

Measurements were conducted as previously described and the resistance measured without the membrane in the cell was subtracted from the resistance measured with the membrane, using a series equivalent for the impedance of the membrane. After this subtraction, the data were converted to parallel values, i.e., conductance and susceptance. The phase angle introduced by the membrane was determined relative to any phase angle measured without membrane. This is important, because the absolute error in the measured phase angle is significantly larger than the relative error between two measurements. The measured phase angles ranged from 0.012° (at 1 mHz) to about 2.9°.

The measured values are presented graphically in Fig. 3 as relative permittivity versus frequency from 1 mHz to 1 kHz. Measured dielectric loss is not plotted as it is totally hidden in the much higher background conductance of the KCl solution. The measured conductance was constant, corresponding to the conductivity of the solution, and this was used to determine the exact uncovered area of the membrane.

As mentioned above, the values for $\delta$ and $\epsilon_\alpha$ are used as adjustable parameters in this paper to make the calculated dielectric dispersion fit the measured data. The fact that the calculated dielectric increment coincides well with the measured data is hence not a proof of the completeness of the theory. Nevertheless, if the nescessary values for $\delta$ and $\epsilon_\alpha$ in order to make the theory fit the measurements are reasonable, the theory is confirmed to be useful for estimating the frequency response to be expected from such measurements.

In Fig. 3, the calculated dispersion was made to fit the measured values by using $\delta = 0.51$ nm and $\epsilon_\alpha = 22$. These values seem sensible and are in agreement with Pethig (4). Using these values, the time constant $\tau = 1.5$, corresponding to a frequency of about 0.1 Hz, and $\kappa b = 9.9$, which justifies the use of flat double layer approximation.

However, a distribution of relaxation times is usually found even in monodisperse systems. Lim and Franses (11) found the distribution parameter $\alpha$ in the Cole–Cole distribution (12) to range from 0.05 to over 0.4 for monodisperse particles in NaCl solution. A higher value for $\alpha$ means that the dispersion covers a larger frequency range. It should therefore be noted that a Cole–Cole distribution of relaxation times with, e.g., $\alpha = 0.05$ would fit the measured data just as well as the single time constant dispersion indicated in Fig. 3.

The measured dispersion was reproducible but the values at 3 mHz and especially 1 mHz were found to vary more than the indicated error bars. Measurements at the lowest frequencies require time constants of several hundred seconds at the output of the lock-in amplifier and stable readings within a phase shift of 0.001° were difficult to obtain with these time constants. The indicated error bars are due to the relative phase error which is only significant at low frequencies. The 1% error in measured values is small in comparison and is not indicated in the figure.

Schwarz (6) introduce $\gamma$ as the relation between the energy gain of a counterion responding to the external field and the energy due to thermal movement, and requires that $\gamma \ll 1$ in his calculations. His expression is

$$\gamma = \frac{e_0 R E}{kT}, \quad [7]$$

where $R$ is the radius of a sphere and $E$ is the electric field. Exchanging $R$ with $\sqrt{a^2 + b^2}$ gives $\gamma = 0.13$ for the experiment presented in this paper.
VI. CONCLUSION

We have found that microporous membranes exhibit low frequency electrical properties in electrolyte solution that most likely are due to counterion relaxation effects. Other mechanisms may contribute to the relaxation, however, and the influence from, e.g., diffusion of ions in the bulk electrolyte, has not been considered in this paper.

A full dispersion was measured using the high accuracy measurements achievable only with modern digital lock-in amplifiers. The membranes used in this paper show a low frequency relative permittivity plateau at about $7 \times 10^5$ and a single dispersion centered at about 0.1 Hz.

We have shown that pores display a capacitance at low frequencies that is higher than the capacitance calculated using the relative permittivity of pure water. The phase angles measured in this experiment were low, however, which may indicate that the sweat ducts are not likely to be responsible for the capacitance of the stratum corneum. This is supported by the fact that saline is more conductive than the solution used here and that the pore density of the skin is much lower than in the membranes. However, no conclusions can be drawn regarding the sweat ducts without information about, e.g., the charge density of the duct walls. This is an interesting topic for further research.

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REFERENCES