Influence of Electrolyte on Electrical Properties of Thin Cellulose Acetate Membranes

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SYNOPSIS

The electrical behavior of thin cellulose-2.5-acetate membranes for chemical semiconductor sensor applications was investigated. The influence of electrolyte on the electrical membrane properties was studied by means of electrochemical impedance spectroscopy. The polymeric membranes can be described using the electrical model of Cole and Cole. The membrane-electrolyte distribution equilibria were investigated by means of an absorption–desorption method using conductivity measurements. The desorption kinetics for thin cellulose acetate membranes differ significantly from those of thicker cellulose acetate reverse osmosis membranes because here the rate of the ionic exchange at the membrane interface cannot be neglected. The experimentally determined distribution coefficients were used for the discussion of the electrolyte influence on the electrical membrane parameters. A functional dependence was found between the specific membrane resistance of cellulose acetate membranes and the ionic hydration enthalpy. The effect of electrolyte on the relative permittivity can be explained by a theoretical model. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The interactions between polymeric membranes and electrolyte solutions have been thoroughly discussed in the literature for many years. Reverse osmosis membranes have been investigated in detail concerning their transport and equilibrium properties as well as electrochemical properties. For example a comprehensive treatment of the problems of distribution equilibria was given by Heyde et al.[1,2] There are many publications dealing with the experimental investigation of diffusion and partition coefficients of various polymeric membranes.[3-5] Comprehensive studies of the electrical behavior of cellulose acetate reverse osmosis membranes were carried out.[6,7]

In the field of ionsensitive field effect transistors, polymeric coatings were used as enzyme and reference sensors.[8-10] For example, polymeric membranes of polyurethane,[8,11] polyvinylpyrrolidone,[9] cellulose derivates,[10,12] polyvinylalcohol,[13] and polyacrylate[11] were applied as diffusion barriers and insensitive layers. Those membranes prepared by means of methods common in semiconductor technology show specific structural characteristics. The very small membrane thickness of about 1 μm and the resulting small proportion between membrane volume and surface can cause properties different from the characteristics of thicker membranes. The material parameters given in the literature differ to a large extent even for membranes of identical polymeric materials depending on the membrane preparation, membrane structure and investigation method. Therefore there is a great demand for a detailed characterization of membranes for special practical applications.

This article deals with the investigation of thin cellulose-2.5-acetate membranes for semiconductor sensor applications. In contrast to studies concerning cellulose acetate reverse osmosis membranes, polymeric layers of an extremely small thickness have to be investigated in this case. In order to investigate the membranes in an unchanged state, the polymeric layers have to be characterized on the solid supporting material to determine the typical membrane properties. The description of the electrolyte influence on the electrical membrane properties is of special interest because these properties directly determine the electrical sensor parameters.

The aim of our work is a systematic description of the electrolyte influence on the electrical behavior of cellulose acetate coatings applied to semiconductor sensors. This was performed on the basis of experimental studies of distribution equilibria for thin polymeric membranes and electrochemical impedance measurements. The experimental results were discussed using complex models of electrical membrane parameters.

EXPERIMENTAL

Membrane Preparation

The polymeric membranes were prepared on gold electrodes and $Si/SiO_2/Si_3N_4$ wafers applying spin-on technology from the following polymeric solution: 2.5 wt % cellulose 2.5-acetate (Inst. f. Polymerchemie Seehof, Germany) in acetone. The membranes were dried for at least 24 h in air at room temperature. The polymeric layers prepared had a membrane thickness between 0.2 and 3.5 μm that was determined using surface profile measurements (taly-step method).

Before investigation the membranes were brought into equilibrium with the aqueous electrolyte solution of interest for a period of time considerably larger than the time necessary for reaching equilibrium (3–24 h).

AC-Impedance Measurements

These measurements were performed using an electrochemical instrument 368 (EG and G, Princeton Applied Research) and an Apple IIe computer. The samples were investigated in a frequency range from 0.3 Hz to 100 kHz. The amplitude of the AC voltage was 5 mV. All measurements were performed using an electrochemical cell with two gold electrodes at the open circuit potential. The membranes were directly prepared on the working electrode (A = 0.5 cm^2) and investigated in the state of equilibrium in different 1M electrolytes. The experimental values were corrected by the impedance of the electrochemical cell.

Investigation of Distribution Equilibrium Between Polymeric Membrane and Electrolyte Phase

The membranes were directly investigated on silicon wafers (covered with 200-nm thick layers of SiO_2 and Si_3N_4). The distribution coefficient was determined by means of an absorption–desorption method. The membranes were brought into equilibrium with a $1M$ aqueous electrolyte solution of interest. The amount of electrolyte absorbed by the polymeric membrane was measured by the desorption into a definite volume of freshly tridistilled water. The increasing salt concentration in the aqueous phase was determined by means of a conductivity measurement. For these measurements an electrochemical conductivity cell with a height of 300 μm was used. The two platinum electrodes were arranged as ring–disk electrodes in the bottom of the cell. The conductivity was measured using a lock-in amplifier (Unipan 232B). A calibration measurement using at least five concentrations of the corresponding electrolyte was carried out after each experiment.

The distribution coefficient of Na^{36}Cl was determined for the cellulose acetate membranes. The amount of electrolyte absorbed by a definite volume of a cellulose acetate membrane was determined by measuring the radioactivity. Calibration samples were prepared from definite amounts of the soak solution. The radioactivity was measured using a radiation measuring equipment including a radiometer 20046 (Meßelektronik Dresden GmbH Vakutronik).

RESULTS AND DISCUSSION

Impedance Spectroscopical Measurements

Electrochemical impedance spectroscopy is a favored investigation method for the characterization of polymeric materials. We used this method for studying the electrical behavior of cellulose acetate membranes of a thickness between 0.2 and 3.5 μm in various electrolyte solutions. The Nyquist-plot (imaginary component Z'' versus real part Z') of a typical impedance spectrum for a cellulose acetate layer is given in Figure 1. The high frequency part of this spectrum can be described by a semicircle with its center below the real axis.

Electrical networks can be used as models for the interpretation of electrochemical impedance spectra. In order to ensure an exact assignment of the individual electrical elements of the network to physicochemical constants and processes, simple electrical circuits have to be chosen. The applicability has to be proved by suitable experiments.

For the systems investigated we found that the impedance is dominated by the bulk of the polymer membrane whereas the interfaces to the electrolyte and the gold can be neglected. Using the well-known
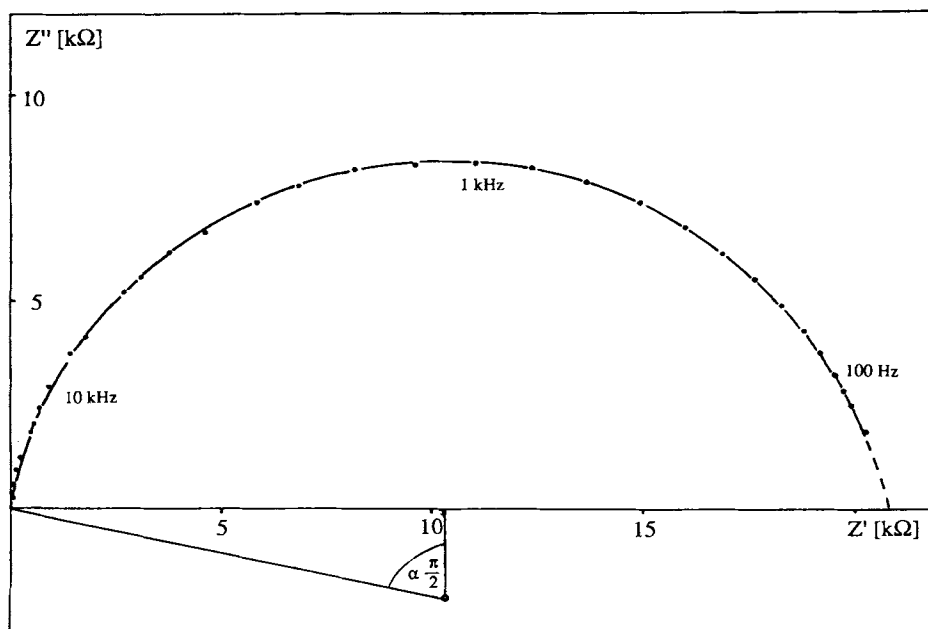
Figure 1   Nyquist-plot of an impedance spectrum of a cellulose acetate membrane in $1M$
Na_2SO_4 solution ($A = 0.5$ cm^2, $d_m = 0.98$ μm; $R_m = 20.72$ kΩ, $C_m = 8.8$ nF, $\alpha = 0.87$).

model of Cole and Cole[14] the bulk properties of the
polymeric membranes used can be described by an
infinite series of parallel RC circuits with time con-
stants showing a random distribution around a mean
time constant τ_m. The mathematical analysis of the
experimental data is possible by means of the Cole–
Cole[14] formula:

$$Z^* = \frac{R_m}{1 + (j\omega R_m C_m)^\alpha} \qquad (1)$$

where C_m, membrane capacity; R_m, membrane re-
sistance; Z^*, complex membrane impedance; α, fre-
quency dispersion; ω, angular frequency. The mem-
brane resistance R_m can be directly determined from
the Nyquist-plot. Using this parameter the geomet-
rical capacity C_m and the exponent α describing the
frequency dispersion can be obtained from the linear
regression of the logarithm of the imaginary part of
admittance against the log ω. The parameter α can
be considered to be a measure for the width of sta-
tistic distribution of the time constants. Therefore
α is directly determined by the homogenity of the
membrane.

Investigating the dependence of the electrical pa-
rameters on the membrane thickness d_m (Fig. 2), a
linear relation was found for the membrane resis-
tance R_m as well as for the reciprocal capacity al-
though there is a wide statistical distribution of the
measured values. Thus it was proved that these pa-

rameters can be used for the description of the
membrane bulk properties. The deviation of the
regression line from the origin is within the error of
the measurements. A significant change of the elec-
trical characteristics within the range of membrane
thickness investigated was not observed. It is pos-
sible to calculate a mean specific resistance and rel-
ative permittivity from the impedance data. The re-
sults are given in Table I.

As shown in Figure 3 and Table I the impedance
spectra of cellulose acetate layers are drastically
changed by the electrolyte. The membrane resis-
tance differs in several orders of magnitude for the
various 1M electrolyte solutions. Also the relative
permittivity changes considerably. The small
changes of the parameter α are overlapped by a wide
statistical distribution of the individual samples. In
the case of KNO_3, NH_4Cl, as well as NH_4NO_3 so-
lutions, the determination of the relative permittiv-
ity and the frequency dispersion was not possible
with sufficient accuracy because of the very low
electrical time constants of the membrane. A de-
tailed knowledge of the distribution and diffusion
properties of the investigated membranes is neces-
sary for the discussion of the effect of electrolytes
on the electrical membrane parameters.

Investigation of Distribution Equilibria

The distribution equilibria were investigated by
means of an absorption–desorption method. The
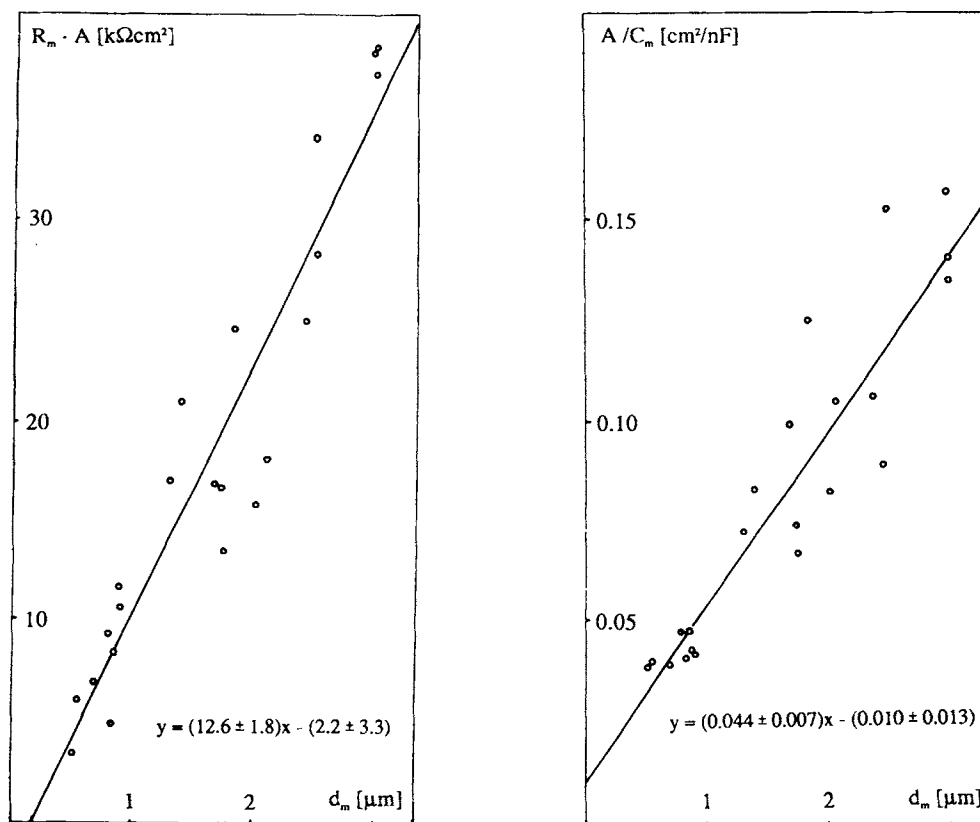
Figure 2 Dependence of membrane resistance and reciprocal capacity of cellulose 2.5-acetate membranes on the membrane thickness.

very small membrane thickness in the range of 200 nm up to 3.5 μm causes an unfavorably low ratio between membrane volume and membrane surface. Furthermore the polymeric layers have to be investigated on the solid supporting material so that the surface area is very limited. To study the uptake of electrolytes, amounts less than 10^{-8} mol have to be detected. Therefore common methods of membrane

characterization are of limited applicability. For the investigation of the thin polymeric layers on solid supporting materials an electrochemical conductivity cell with a volume of 30 μL was developed (see also Experimental).

The mean distribution coefficients of some selected salts for cellulose acetate membranes are given in Table II. Compared with distribution coef-

Table I   Electrical Parameters of Cellulose 2.5-Acetate Membranes in Different 1M Electrolytes

Electrolyte System	ρ_m (Ω cm)	ε_m	τ_m (s)	α
NaCl	$(1.10 \pm 0.36) \cdot 10^6$	28.7 ± 3.7	$(2.8 \pm 1.3) \cdot 10^{-6}$	0.82–0.85
NaNO$_3$	$(2.70 \pm 0.59) \cdot 10^5$	30.1 ± 2.3	$(7.2 \pm 2.1) \cdot 10^{-7}$	0.80–0.84
NaF[a]	$(8.80 \pm 1.80) \cdot 10^6$	25.7 ± 4.0	$(2.0 \pm 0.7) \cdot 10^{-5}$	0.80–0.87
Na$_2$SO$_4$	$(1.26 \pm 0.18) \cdot 10^8$	25.4 ± 1.1	$(2.8 \pm 0.5) \cdot 10^{-4}$	0.85–0.88
CaCl$_2$	$(3.09 \pm 0.20) \cdot 10^7$	30.0 ± 2.9	$(8.2 \pm 1.3) \cdot 10^{-5}$	0.83–0.87
Ca(NO$_3$)$_2$	$(1.49 \pm 0.19) \cdot 10^6$	25.9 ± 3.4	$(3.4 \pm 0.9) \cdot 10^{-6}$	0.80–0.85
CuSO$_4$	$(5.60 \pm 1.10) \cdot 10^7$	29.3 ± 3.1	$(1.5 \pm 0.4) \cdot 10^{-4}$	0.82–0.90
KCl	$(5.20 \pm 1.10) \cdot 10^5$	29.9 ± 3.5	$(1.4 \pm 0.5) \cdot 10^{-6}$	0.80–0.84
KNO$_3$	$(2.13 \pm 0.63) \cdot 10^5$			
NH$_4$Cl	$(4.55 \pm 0.57) \cdot 10^5$			
NH$_4$NO$_3$	$(1.26 \pm 0.44) \cdot 10^5$			

[a] Concentration 0.3 mol/L.
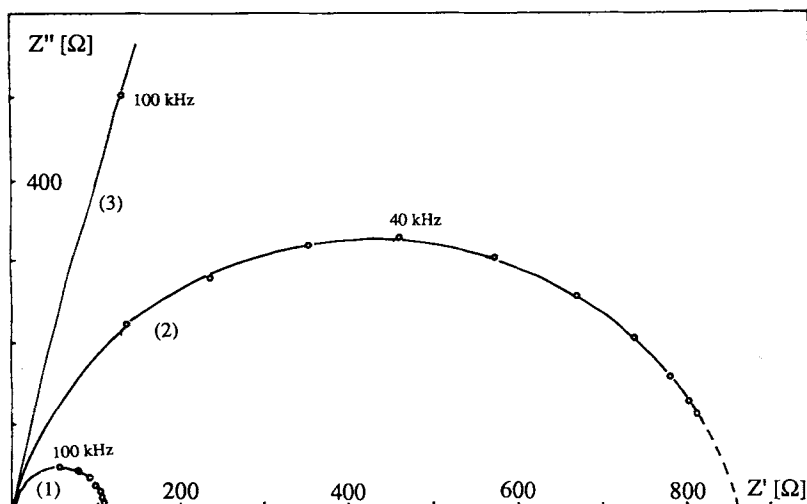
Figure 3 Impedance spectra of a cellulose acetate membrane in different 1M sodium electrolyte solutions: 1, Na_2SO_4; 2, NaCl; 3, $NaNO_3$; $d_m = 1.7$ μm; $A = 0.5$ cm^2; (1)R_m = 41.2$k\Omega$; $C_m = 5.6$ nF; $\alpha = 0.87$; (2)$R_m = 870\Omega$, $C_m = 6.9$ nF, $\alpha = 0.82$; (3)$R_m = 114\Omega$, C_m = 8.9 nF, $\alpha = 0.8$.

ficients determined for thicker reverse osmosis membranes, the values obtained are remarkably high. Partition coefficients for cellulose 2.5- acetate membranes[5] were obtained by an analogous conductivity method. These values are about three times smaller than our experimental data. The distribution coefficient of NaCl was additionally measured by an independent tracer method. Using this method a value of $K = 0.19 \pm 0.06$ was determined. Although the experimental error of this method is also relatively high, the given magnitude of the distribution coefficient was corroborated by these experiments. The differences between our experimental values and the data given in the literature can be explained by the special structure of the very thin membranes prepared by means of the spin-on technology. So we assume that the volume fraction of water is high compared with reverse osmosis membranes.

An increase in the partition coefficient was found for increasing ionic radius and decreasing valency. These effects of ionic size and charge on the distribution equilibrium corresponds well to the influences discussed in the literature.[1,5] A theoretical approach for this phenomenon was given by Glueckauf.[15] The

distribution of inorganic ions is mainly governed by the effect of dielectric exclusion. On the basis of the calculation of the energy difference between the ion in the solution and the ion in an aqueous pore of the membrane, the probability of finding an ion in this pore can be determined. So the following equation was derived for the thermodynamic distribution coefficient K^* (K^* is defined here as the ratio between the ion concentration of the aqueous solution in the membrane and the ion concentration of the external solution):

$$K^* = \exp\left[\frac{e^2 z^2}{-2\varepsilon_1 kT} \cdot \frac{(1-\chi)Q}{r + \chi bQ}\right] \quad (2)$$

$$\chi = 1 - \frac{1}{\sqrt{1 + K_{DH}^2 r^2}} \quad (3)$$

where b, ionic radius; e, elementary charge; k, Boltzmann constant; K^{DH}, inverse Debye length; K^*, thermodynamic distribution coefficient; $Q = (\varepsilon_1 - \varepsilon_2)/\varepsilon_1$; r, pore radius; T, temperature; z, ionic valency; ε_1, dielectric constant of the aqueous phase;

Table II   Distribution Coefficients of Different Electrolytes for Cellulose 2.5-Acetate Membranes

	Na_2SO_4[a]	NaF[b]	NaCl[a]	$NaNO_3$[a]	NH_4NO_3[a]
K	0.01 ± 0.003	0.10 ± 0.05	0.12 ± 0.02	0.25 ± 0.04	0.35 ± 0.04

[a,b] $K = c_{membrane}/c_{solution}$, electrolyte concentrations: [a]1 mol/L, [b]0.8 mol/L.

Table III   Calculation of Distribution Coefficients of Selected Anions

	NO_3^-	Cl^-	F^-	SO_4^{2-}
b (nm)	0.230	0.181	0.133	0.233
K^*	0.293	0.248	0.200	0.064

$\epsilon_1 = 78$, $\epsilon_2 = 4$, $c_{\text{solution}} = 1$ mol/L, $r = 3$ nm.

ϵ_2, dielectric constant of the polymer. The partition coefficients of the concerned ions calculated for a membrane pore radius of 3 nm are given in Table III. Although the experimentally observed tendencies can be explained by means of this model, it is not possible to fit the mean distribution coefficients of the investigated electrolytes if the parameter were varied in a suitable range. This may be caused by simplifications made in this model. The formation of ionic pairs, that is especially important for electrolytes of high concentration, is not considered. Furthermore fixed charges of the membranes that are also influencing distribution equilibria of ions are neglected. Nevertheless the model of Glueckauf [15] can be used for a qualitative discussion of dependence of the distribution coefficient on individual ionic characteristics.

## Discussion of Kinetics of Electrolyte Desorption

During the experiments for the determination of the distribution coefficients, an increasing electrolyte concentration in the aqueous phase was registered. Therefore a discussion of the kinetics of these desorption processes was possible. Significant differences of the desorption rate were found for the individual salts (Fig. 4).

Commonly it is possible to analyze analogous experiments concerning the kinetics of the electrolyte transport using a simple diffusion model as described by Lonsdale et al.[5] Assuming Fickian behavior, the diffusion into or out of a semiinfinite membrane of the thickness Δx can be described using the following equation[16]:
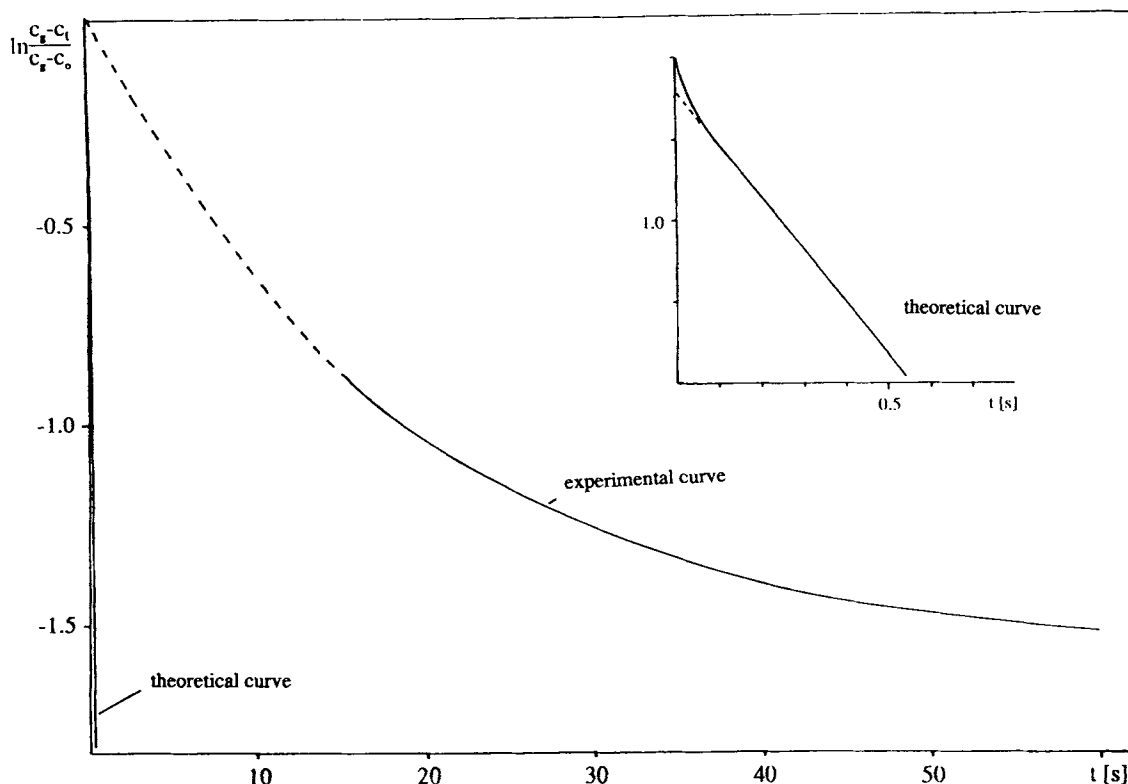
$$\frac{c_f - c_t}{c_f - c_0} = \frac{8}{\pi^2} \cdot \sum_{\nu=0}^{\infty} \frac{1}{(2\nu + 1)^2}$$

$$\times \exp\left[-(2\nu + 1)^2 \cdot \frac{\pi^2 D t}{\Delta x^2}\right]. \quad (4)$$

The higher order terms of the sum can be neglected for times of $t \geq 0.1\Delta x^2/\pi^2 D$, so that the equation can be reduced to:

$$\frac{c_f - c_t}{c_f - c_0} = \frac{8}{\pi^2} \cdot \exp\left[\frac{\pi^2 D t}{\Delta x^2}\right] \quad (5)$$
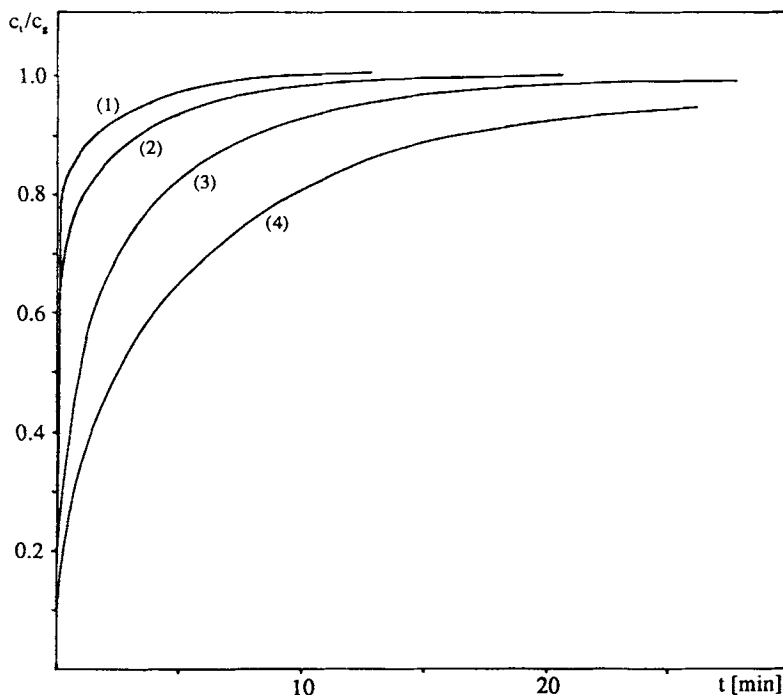
Figure 4   Kinetic of desorption of different electrolytes: 1, NH_4NO_3; 2, $NaNO_3$; 3, NaCl; 4, Na_2SO_4; 1–3: $d_m = 0.6$ μm; 4: $d_m = 1.4$ μm.

Figure 5   Experimentally registered desorption of $NaNO_3$ ($d_m = 0.6 \mu m$) compared with a theoretical curve according to eq. (6).

where c_0, initial concentration; c_f, equilibrium concentration; c_t, concentration for time t; D, diffusion coefficient; t, time; Δx, membrane thickness. According to this equation the diffusion coefficient can be determined from the slope of the plot of $\ln[(c_f - c_t)/(c_f - c_0)]$ versus time t. Because only relative concentrations are required, the measured solution conductivities can be used directly.

In Figure 5 an experimental curve for the desorption process of $NaNO_3$ out of a 0.6-μm cellulose acetate membrane was compared with a theoretical one calculated for the given membrane thickness and using the mean diffusion coefficient of $NaNO_3$ determined by Lonsdale et al.[5] From this figure it can be seen that the desorption process is considerably slower than was assumed from the diffusion coefficients given in the literature. A concentration of 90% of the equilibrium concentration is reached in a time of about 3 min, whereas the theoretical calculated time is 0.65 s. Furthermore it has to be pointed out that the shape of the experimental curve deviates remarkably from a straight line. Therefore we conclude that the very thin cellulose acetate membranes show distinguishing characteristics concerning the kinetics of sorption and desorption

of electrolyte. For that reason the diffusion model proposed seems to be unapplicable for the description of the desorption kinetics for these membranes.

Investigating the desorption process for membranes of various thicknesses, it was found that the change in the desorption rate is remarkably smaller then can be calculated for a diffusion process. According to eq. (5) the time necessary for reaching a definite part of the final concentration is proportional to $(d_m)^2$. In contrast to this we found a nearly linear relation to the membrane thickness. From these results we assume that the process of ion exchange at the interface membrane–electrolyte has to be taken into account in the discussion of the kinetics of the whole electrolyte desorption process for very thin membranes. Consequently a direct determination of the diffusion coefficients is not possible in contrast to the measurement of distribution coefficients.

One model describing the connection of membrane–electrolyte interactions and electrical membrane properties like membrane resistance is the equation of Schlögl.[17] Neglecting the convective term of electrical membrane conductance this equation can be simplified to the following relation:

$$\rho = \frac{RT}{F^2} \cdot 1 / \sum_i z_i^2 c_i D_i \qquad (6)$$

where c_i, concentration of the ion in the membrane phase; D_i, diffusion coefficient of the ion in the membrane phase; F, Faraday constant; R, gas constant; T, temperature; ρ, specific membrane resistance. On the basis of this equation diffusion coefficients can be calculated from the experimentally determined membrane resistances (Table I) and distribution coefficients (Table II). The results for 1-1-electrolytes in cellulose-2.5-acetate are given in Table IV. These resulting values are in the range of diffusion coefficients given in the literature[7,18] that vary from about $0.89 \cdot 10^{-9}$ cm^2/s up to $5.1 \cdot 10^{-9}$ cm^2/s. The tendency of changes in the diffusion coefficient caused by the individual cation and anion effects agrees well with other results.[5]

Discussion of Electrolyte Influence on Electrical Membrane Properties

As proved by the impedance spectroscopical investigation, the electrical characteristics of cellulose acetate membranes are strongly dependent on the electrolyte solution. These effects will be discussed on the basis of theoretical models in the following.

The correlation of electrical membrane parameters with general characteristics of the electrolyte solution was one intention of our experimental studies. On the basis of the sorption–capillary flow model for reverse osmosis membranes, an empirical expression for the membrane selectivity was found by Dytnerskij.[19] This equation describes the dependence of the membrane selectivity referring to a given salt on the hydration properties of the individual ions:

$$\log(1 - \phi) = A - B \cdot \log(\Delta_H H_1 \cdot \Delta_H H_2^m) \qquad (7)$$

where A, B, empirical constants; $\Delta_H H$, hydration enthalpy of the ion; m, experimental parameter; ϕ, selectivity constant. The constants $\Delta_H H_1$ and $\Delta_H H_2$ are the hydration enthalpies of the anion and cation with the greater value $\Delta_H H_2$. The factor m is a parameter experimentally determined by Dytnerskij[19]

describing the interaction of both ions. Therefore m is a function of the ionic valencies. We found an analogous function for the dependence of the specific membrane resistance of the cellulose acetate membranes on the hydration properties of the electrolyte system (Fig. 6). It should be mentioned that the applicability of this mathematic function is very limited. It can only be used for high concentrations of the electrolyte system because the influence of fixed charges can be neglected under these conditions.

Not only the membrane resistance but also the relative permittivity is affected by the absorption of electrolyte. A model describing the capacitance of a disperse system of an insulating continuous phase and conducting disperse phase was developed by Trukhan.[20] This model is only valid for a small volume fraction of the disperse phase. The concept was further developed by Malmgren–Hansen et al.[7] using the integration method of Brüggemann.[21] The mathematical expression derived is applicable for larger volume fractions as high as 0.5.

$$\left[\frac{\varepsilon_1 - \varepsilon_m(1 - \beta)}{\varepsilon_1 - \varepsilon_2(1 - \beta)} \right] \cdot \frac{3\varepsilon_2}{\varepsilon_m} = (1 - \Phi)^3 \qquad (8)$$

$$\beta = \frac{[3 + (\kappa_{DH} a)^2] \tanh(\kappa_{DH} a) - 3\kappa_{DH} a}{[2 + (\kappa_{DH} a)^2] \tanh(\kappa_{DH} a) - 2\kappa_{DH} a} \qquad (9)$$

where a, radius of alveolus; κ_{DH}, inverse Debye length; ε_1, relative permittivity of the disperse phase; ε_2, relative permittivity of the continuous phase; ε_m, relative permittivity of the membrane; Φ, volume fraction of water. This mathematical function was used for the calculation of the theoretical dependence of the relative permittivity of the cellulose acetate membrane on the ionic strength of the electrolyte solution (Fig. 7). In this context the inverse Debye-length κ_{DH} was used for the description of the disperse phase of the membrane. Therefore the membrane capacity is a function of the ionic strength within the pores of the membrane. It can be seen that this model is able to account for the experimentally determined changes of the membrane capacity caused by different salts in the elec-

Table IV   Calculated Diffusion Coefficients for Different Electrolytes

|	NaNO$_3$	NaCl	NaF	Na$_2$SO$_4$	NH$_4$NO$_3$
D (cm^2/s)	$2.0 \cdot 10^{-9}$ [a]	$1.1 \cdot 10^{-9}$ [a]	$0.5 \cdot 10^{-9}$ [b]	$3.5 \cdot 10^{-11}$ [a]	$3.0 \cdot 10^{-9}$ [a]

[a] 1 mol/L; [b] 0.3 mol/L.
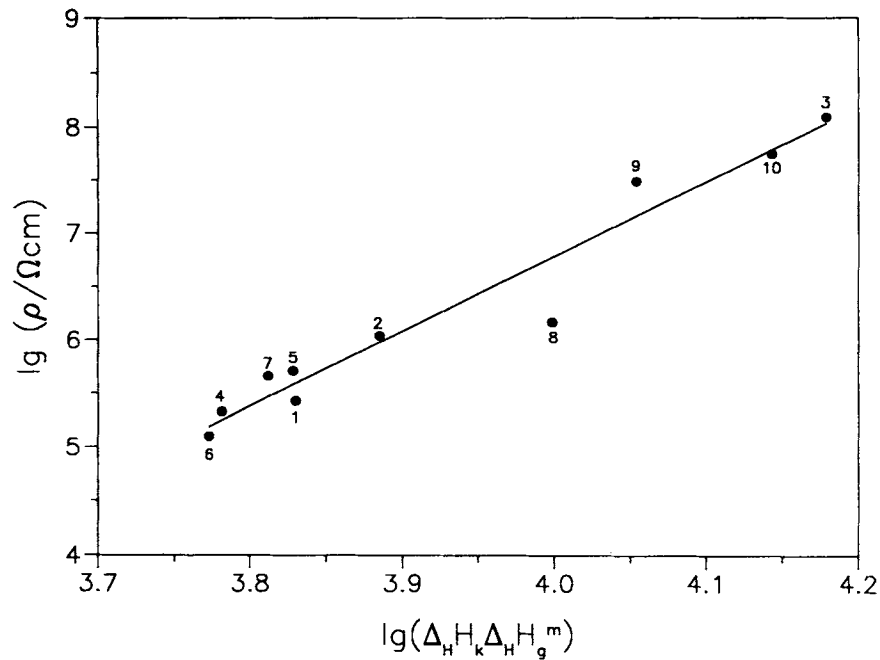
Figure 6 Functional dependence of the specific membrane resistance on a function of the molar hydration enthalphies of the ions (hydration enthalpies[22] are given in kJ/mol from of the concerning electrolytes: 1, $NaNO_3$; 2, NaCl; 3, Na_2SO_4; 4, KNO_3; 5, KCl; 6, NH_4NO_3; 7, NH_4Cl; 8, $Ca(NO_3)_2$; 9, $CaCl_2$; 10, $CuSO_4$.

trolyte. The experimental values were obtained by a correlation of the experimentally determined distribution coefficients and relative permittivities.

Additionally an effect of the sorption of electrolyte on the frequency dispersion has been observed. The parameter α decreases with increasing uptake
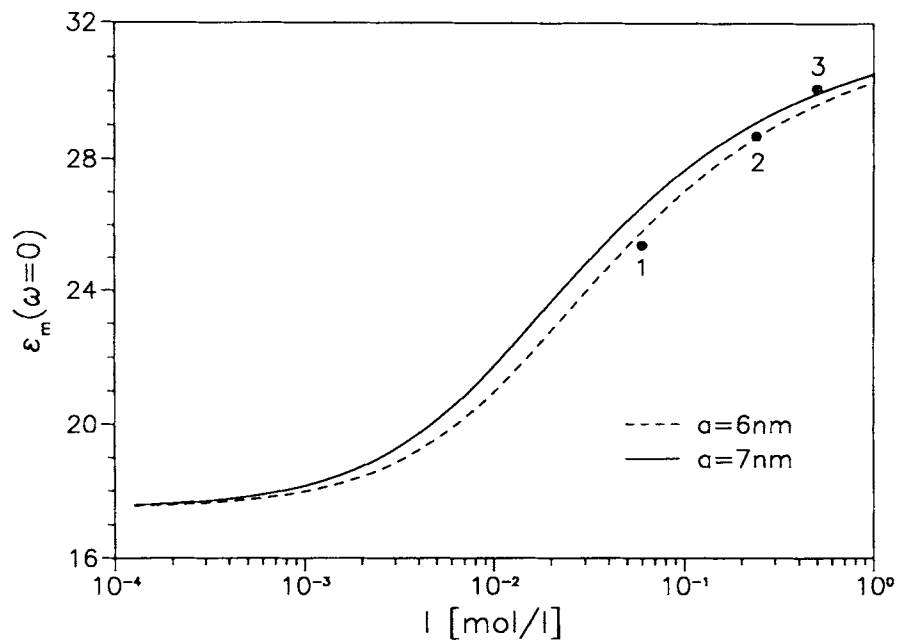
Figure 7 Comparison between the theoretical dependence of the relative membrane permittivity and the ionic strength in the aqueous phase of the membrane according to eq. (8) and experimental results for: 1, Na_2SO_4; 2, NaCl; 3, $NaNO_3$ (Tables I and II); Φ = 0.5; ε_1 = 78; ε_2 = 4.

of electrolytes. This fact corresponds to the idea of decreasing homogeneity if smaller pores are also involved in the absorption of ions.

CONCLUSIONS

The electrical behavior of thin cellulose 2.5-acetate membranes can be described using the well-known electrical model of Cole and Cole.[14] The specific membrane resistances and relative permittivities are strongly affected by the electrolyte solution. This can be explained on the basis of a distribution equilibrium between polymeric membrane and electrolyte solution. The distribution coefficients for the individual salts decrease with decreasing ionic size and increasing ionic valencies. These tendencies can be explained by means of the theoretical approach of Glueckauf.[15]

The change in the relative permittivity for cellulose 2.5-acetate membranes in different electrolytes can be described using the mathematical equation of Malmgren–Hansen et al.[7] which is based on the theoretical model of Trukhan.[20] Experimental values obtained by correlation of measured partition coefficients and relative permittivities are in good agreement with the theoretical function. A functional dependence between the specific resistance and the hydration enthalpy of the individual ions was observed.

From our desorption measurements we conclude that the desorption kinetics are determined by the ion exchange at the interface. Therefore these experiments cannot be analyzed using simple diffusion models. Diffusion coefficients of different electrolytes were calculated from the experimentally determined membrane resistances and distribution coefficients (Table IV). The calculated values are in the range of diffusion coefficients reported for cellulose acetate.[5,7,18] The effect of the ionic size on the diffusion coefficient agrees well with tendencies described by Lonsdale et al.[18]

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