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Impedance spectroscopy and surface study of potassium-selective silicone rubber membranes

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Abstract

Impedance spectroscopy measurements of silicone rubber membranes containing potassium-selective neutral carriers are reported. Two types of silicone rubbers are studied viz. the commercially available Siloprene and a novel copolymer, that was synthesized for application on Ion-Sensitive Field Effect Transistors (ISFETs). Three different potassium-selective ionophores have been studied, the natural ionophore, valinomycin, and two hemispherand type ionophores. One of the hemispherands can be covalently bonded to the polysiloxane copolymer matrix. The bulk resistance of the valinomycin containing membranes was found to be dependent on the contacting electrolyte solution. The K^+/Na^+ selectivity of the membrane is reflected in the behavior of the bulk resistance. The presence of a surface film on Siloprene membranes reported in the literature is confirmed. A surface study revealed the presence of small droplets exuded by the Siloprene membrane. The copolymer seems not to suffer from the presence of a surface film.

INTRODUCTION

Potassium-selective neutral carrier membrane electrodes containing valinomycin in a plasticized PVC-matrix have been used successfully for many years. Although this electrode normally functions very well, there are some specific applications where the use of alternative membrane materials offers distinct advantages. For example in the determination of potassium in biological samples the use of silicone

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rubber matrices is beneficial in minimizing the interference of lipophilic anions [1,2].

Also the modification of ISFETs requires the use of alternative membrane materials. The problems that are encountered with the application of plasticized PVC-membranes on ISFETs include the loosening of the physically adhered membrane, the leaching out of electroactive components (solvent mediator, ionophore, and anionic sites) from the thin membranes, CO₂ interference, and the technological difficulties related with the membrane deposition and the encapsulation of the devices. In the last few years we have developed a strategy to overcome these problem [3–7]. Our research is focussed on the development of new membrane materials which can be applied to the ISFET surface using photolithographic techniques. Furthermore the resulting membrane must be linked covalently to the ISFET surface and should not suffer from the leaching out of electroactive material.

For this purpose polysiloxane copolymers containing methacrylate groups and a hemispherand ionophore, functionalized with a methacrylate group have been synthesized. During the radical crosslinking reaction the ionophore is presumed to bind covalently to the membrane matrix. This crosslinking reaction can be achieved using photolithography. The performance and lifetime of CHEMFETs modified with these membrane materials are good [7]. After 140 days of exposure to electrolyte solutions a Nernst slope of 52 mV/dec. was maintained.

An observed limitation however, is the high membrane resistance which limits the membrane thickness and results in a high noise level of the sensor. For further improvement of the membrane materials it is necessary to characterize the physical properties of the membrane such as the membrane resistance and the dielectric constant.

The mechanism and properties of PVC based membranes, in particular membranes containing valinomycin have been studied extensively, two recent review articles [8,9] summarize the most recent overall picture. ac-Impedance spectroscopy has proved to be a versatile technique in the study of these PVC membranes. The impedance method has been used successfully in separating surface rates from bulk rates of transport [10,11]. Evidence was found for the presence of an exuded plasticizer or surfactant layer on some PVC membranes. The electrical and dynamic properties of polysiloxane Siloprene membranes containing valinomycin have been reported recently [12]. In that study the impedance characteristics of Siloprene and the response time of Siloprene electrodes to activity steps at membrane surfaces have been related. It was concluded that Siloprene membranes also suffer from the presence of a high resistance surface film; this film causes a slower response to activity steps at the membrane surface. The existence of a surface resistive layer makes it very difficult to study the real interfacial properties of the plasticized PVC and Siloprene membranes.

In this paper the impedance characteristics of Siloprene membranes and of a novel polysiloxane copolymer are reported. The copolymer is specially designed for the modification of CHEMFETs. The first results indicate no evidence for the

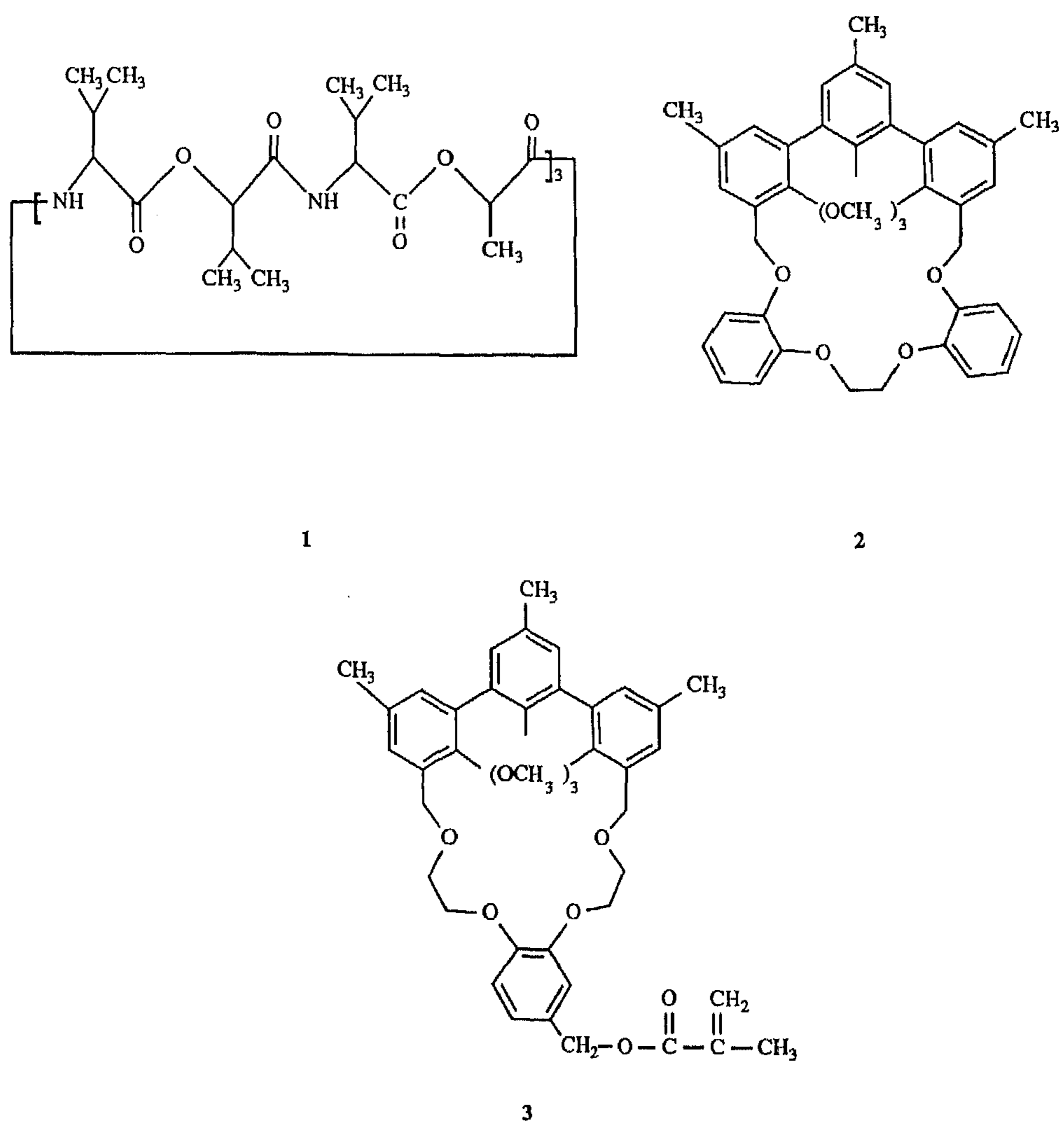


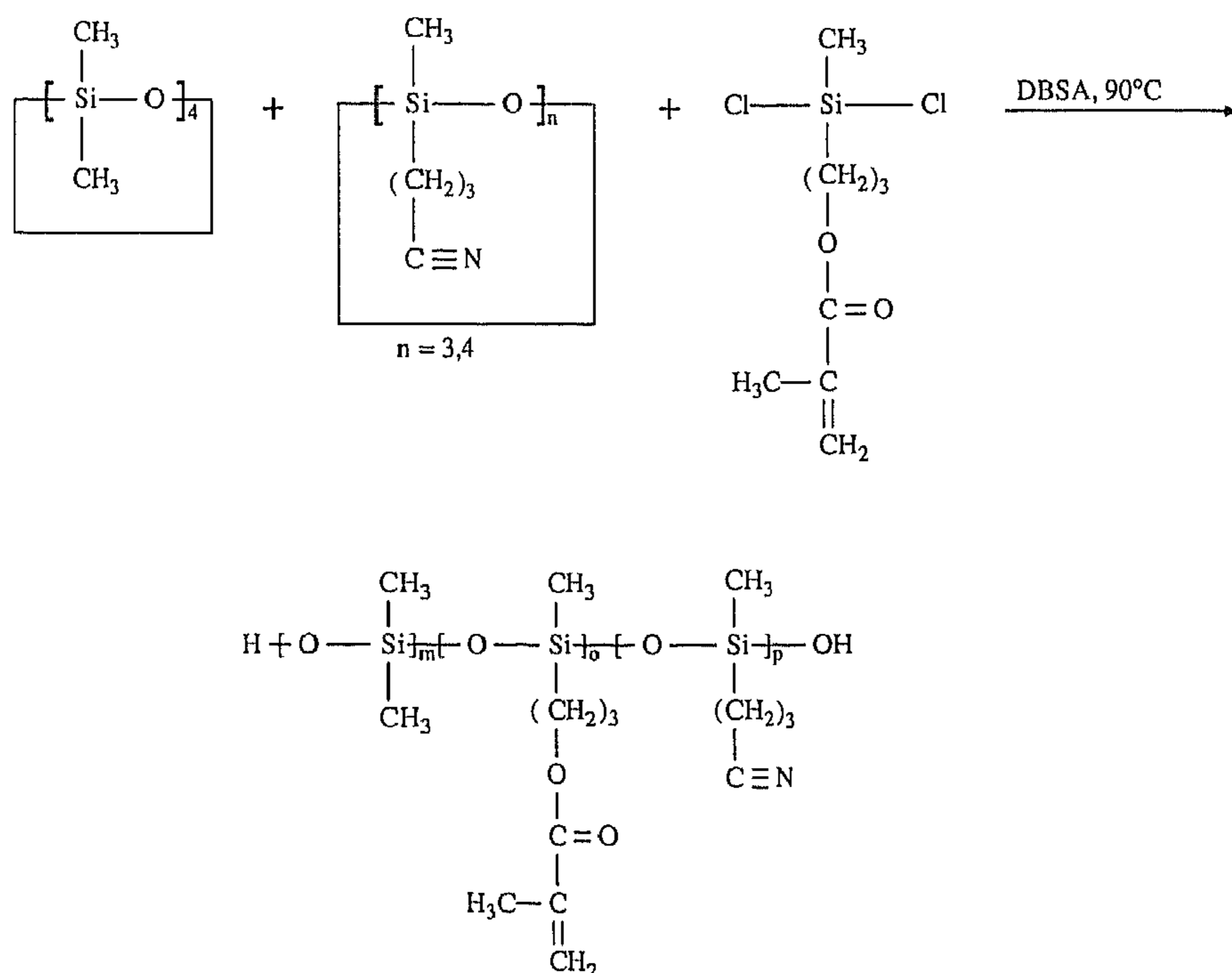
Fig. 1. Structural formulae of the neutral ionophores investigated.

presence of a high resistance surface layer on this copolymer. The ionophores used in this study are valinomycin (1), diphenyl hemispherand-21 (2), and methacryloylphenyl hemispherand-21 (3) (see Fig. 1). In addition the membrane surfaces were studied by optical microscopy.

EXPERIMENTAL

Chemicals

Silanol terminated polydimethylsiloxane Siloprene K-1000 and Siloprene crosslinking agent K-11 were purchased from Fluka. The synthesis of the copoly-



Scheme 1. The synthesis of the copolymers of (cyanopropyl)methyl-, (methacryloxypropyl)methyl-, and dimethylsiloxane $m:o:p = 97.6:1:1.4$.

mers of (cyanopropyl)methyl-, (methacryloxypropyl)methyl-, and dimethylsiloxane is outlined in Scheme 1. The starting mixture contained 2.8 mol% (3-cyanopropyl)methylsiloxane (a mixture of the cyclic trimer and tetramer), 1.4 mol% methacryloxypropylmethylchlorosilane, and 95.8 mol% octamethyltetracyclosiloxane and the polymerization was carried out as described before [6]. The mol% corresponds with the amount of the specific siloxane unit. From ^1H NMR and elemental analysis data it was concluded that the resulting polymer contained 1.4 mol% (3-cyanopropyl)methylsiloxane and 1.0 mol% methacryloxypropylmethylsiloxane units. All the reactants were purchased from Petrarch Systems.

2,2'-Dimethoxy-2-phenylacetophenone (Janssen Chimica) was used as the photoinitiator.

Valinomycin was purchased from Fluka, the syntheses of the diphenylhemispherand (2) [4] and the methacryloylphenylhemispherand (3) [7] have been described elsewhere.

The complex of the ionophore and potassium tetrakis(4-chlorophenyl)borate, $\text{KB}(\phi\text{Cl})_4$ (Fluka) was prepared by shaking both components in methylene chloride (HPLC-grade, Aldrich) for 3–4 hours; in all cases a clear solution was obtained.

The PVC membranes used for surface studies were made by solvent casting from tetrahydrofuran (THF). High molar mass PVC and bis(2-ethylhexyl)sebacate (DOS) were purchased from Fluka, THF was freshly distilled before use.

All solutions were prepared in deionized water, treated in a MilliQ-plus installation from Waters. The potassium chloride used was of p.a. grade and the sodium chloride was of suprapur quality (Merck-Schuchardt).

Membranes

Siloprene K-1000 is a silanol terminated polydimethylsiloxane. Both Siloprene K-1000 and the copolymer can be cross-linked via a condensation reaction of the silanol end groups with tetraethoxysilane present in the cross-linking agent K-11 [5]. The copolymer synthesized here, contains two additional building blocks i.e. a (3-cyanopropyl)methylsiloxane and a methacryloxypropylmethylsiloxane which serve the following purposes: (i) By changing the number of cyanogroups, the dielectric constant of the membrane can be tuned to an optimal value. This value is characterized by a low membrane resistance and a good selectivity of the electrode. Membranes with a high dielectric constant are preferred for divalent cation-selective electrodes, and membranes with a low dielectric constant for monovalent cation-selective electrodes. (ii) The methacrylate groups can be used for the crosslinking of the polymer via a radical reaction mechanism by irradiation with UV light in the presence of a suitable photoinitiator. The preparation of the membranes is described below, the compositions of the various membranes are given in Table 1.

Membranes crosslinked via photochemically induced radical reaction

A solution was made of the copolymer (350–400 mg), the photoinitiator (11–12 mg), and a mixture of the free ionophore and the $\text{KB}(\phi\text{Cl})_4$ -ionophore complex (~ 1:1) in 3 ml of methylene chloride. This solution was poured into a glass ring (diameter: 5 cm) which rested on a flat glass plate. The solvent was allowed to evaporate for at least 2 h in a clean environment. Finally the membrane material was exposed to UV light (100 W high pressure mercury lamp, Blak-Ray B-100A) in a nitrogen atmosphere for at least 10 min. The distance between the lamp and the glass plate was approximately 10 cm.

Membranes crosslinked via a condensation reaction

The crosslinking agent K-11 (30–35 mg), dissolved in 0.5 ml of methylene chloride was added to the silanol terminated polysiloxane (300–350 mg) and a mixture of the free ionophore and the $\text{KB}(\phi\text{Cl})_4$ -ionophore complex (~ 1:1) dissolved in 2.5 ml of methylene chloride. The obtained solution was mixed thoroughly and poured into a glass ring (diameter: 5.0 cm) which rested on a flat Teflon plate. The solvent was allowed to evaporate in a clean environment with a clean beaker covering the ring.

The membranes were carefully loosened from the underlying plate. In some cases this was extremely troublesome and had to be done in a waterbath to prevent the membrane from sticking to itself. The membranes were either stored floating in this waterbath, or used immediately and positioned in the measuring cell. The thickness was determined after all the measurements were performed. This was done by cutting out of a small strip of the membrane and positioning it vertically in a holder. The thickness was measured by means of a microscope with a measuring eyepiece. The overall membrane thickness varied between 100 and 180 μm , while the thickness of the individual membranes was constant within 10 μm . The microscope, also used for the surface study of the membranes, was an Olympus BHSM metallurgical microscope.

Apparatus

Typically, a membrane was placed between two identical halves of the measuring cell which, after mounting in a frame, was placed in an earth-connected metal box. Coaxial cables were used for connecting the electrodes. The Perspex measuring cell used was equipped with four chloridized silver gauzes (diameter: 2 cm, 64 meshes/ cm^2) as electrodes. The silver gauzes were chloridized chemically by exposure to a solution containing 0.3 g NaCl, 0.3 g Na_2HPO_4 , 2 ml water, and 5 ml household bleach for 6–8 min. The electrodes were placed parallel to the membrane, at a distance of about 0.5 and 5 cm on both sides of the membrane. The active membrane area exposed to the electrolyte solution was 1.77 cm^2 .

The ion-selective properties of the membranes were checked by asymmetric filling of the measuring cell with 0.1 M KCl and 0.1 M NaCl solutions and measuring the potential difference between the two identical electrodes on either side of the membrane. A Philips PW9421 pH/mV meter recorded potential differences of 180–200 mV for the hemispherand containing membranes and 220–250 mV for the valinomycin containing membranes.

The impedance measurements were performed over the frequency range of 0.1 MHz–10 mHz using a Solartron 1255 frequency response analyser and a Solartron 1186 electrochemical interface, controlled by an AT80286 personal computer. The impedance spectra were analyzed with the help of the "EQUIVALENT CIRCUIT" nonlinear least squares fit program [13,14].

During these measurements it became clear that a rather high amplitude (0.5 V) was needed to prevent noisy spectra. Because of the high membrane resistances several measurements using different values for the standard resistance in the appropriate frequency part of the spectrum had to be performed. Due to the decrease in the cell impedance with increasing frequency, the low frequency part of the spectrum could best be studied with a high standard resistance (10 M Ω for membranes **R1**, **R2**, **R3**, **R4**, and **C2**, 100 k Ω for membrane **C1**), and the high frequency part with a substantially lower standard resistance (10 k Ω for all membranes). This was confirmed by measurements with an electronic circuit consisting of a parallel capacitor and resistance of 100.8 pF and 10.4 M Ω , respectively. The most reliable value for the membrane resistance was obtained

from the low frequency part of the spectrum and the capacitance from the high frequency part.

RESULTS AND DISCUSSION

ac-Impedance measurements

General features

In a debate in the literature about the significance of measured exchange current densities [15,16] Armstrong pointed out that ac-impedance studies should be performed with membranes contacting only one type of electrolyte solution and that only one type of salt should be allowed to exchange between the membrane phase and the electrolyte phase. A membrane containing e.g. $\text{NaB}(\phi)_4$ should contact only sodium salt solutions, because when this membrane contacts a potassium salt solution, the mixed cation exchange processes will result in complex ac-impedance spectra. However, in our study the mechanical strength of the membranes was insufficient for many manipulations, so whenever a membrane could be placed undamaged in the measuring cell, as many measurements as possible were done with the same membrane. In order to prevent erroneous interpretations of the impedance spectra because of the above mentioned effect, several subsequent measurements were performed whenever the contacting salt solution was changed in order to see how the impedance spectra changed in time. In this way also a more realistic picture is presented, because in laboratory use the membrane will be exposed to salt solutions of variable composition.

It should be noted that all membranes showed the presence of crystallites. This implies that the membranes studied are two phase systems. The concentration of the ionophore/complex in the silicone rubber phase is not known, but it will be at the saturation level, so membranes containing different amounts of ionophore (crystals) will have the same concentration of ionophore. The amount and size of the crystallite phase is also unknown and perhaps variable. The influence of this second phase on the impedance spectra was not an object of this study. Although we realize this may not be a correct assumption, the influence is assumed to be equal for all membranes.

Material properties

The membrane compositions used, the bulk resistivities ρ , and the dielectric constants ϵ are given in Table 1.

The copolymer membrane **R1**, containing valinomycin and crosslinked through a radical reaction, is a membrane without $\text{KB}(\phi\text{Cl})_4$. As expected this membrane initially has a very high resistance. After several days of conditioning in 0.1 M KCl however, the membrane resistance drops to a value of the same order of magnitude as the resistance of membrane **R2**, a membrane of the same composition but containing $\text{KB}(\phi\text{Cl})_4$. Also the final dielectric constant of both membranes is similar. This indicates that the final amount of charge carriers hardly differs and

TABLE I
Membrane composition (% w/w) and selected properties

Membrane components and properties	Membrane ^a					
	R1	R2	R3	R4	C1	C2
Siloprene-K1000	–	–	–	–	–	90.1
Copolymer ^b	96.4	95.9	96.5	95.5	90.6	–
Crosslinking K-11	–	–	–	–	8.5	8.9
Photoinitiator	2.7	3.5	2.4	3.4	–	–
Ionophore ^c	0.90 (1)	0.48 (1)	0.86 (2)	0.83 (3)	0.72 (1)	0.84 (1)
KB(ϕ Cl) ₄	–	0.12	0.24	0.27	0.18	0.16
$\rho(t = 0)$ ^d /10 ⁸ cm Ω	250–500		35–40		6–8.5	60–70
$\rho(t > 7 \text{ days})$ ^d /10 ⁸ cm Ω	35–50	20–35	25–30	20–40	1.5–2.5	25–35
ϵ ^e	10–12	9–11.5	7.5–11.5	7.5–10	5–7 ^f	2.5–4.5

^a **R**: membrane crosslinked via a Radical reaction; **C**: membranes crosslinked via a Condensation reaction.

^b Copolymer of dimethyl(cyanopropyl)methyl(methacryloxypropyl)methyl siloxane.

^c **1**: valinomycin; **2**: diphenyl hemispherand-21; **3**: methacryloylphenyl hemispherand-21.

^d Bulk specific resistance at time t .

^e Dielectric constant.

^f When exposed to NaCl solutions $\epsilon = 11$.

the contribution of the chloride anion to the membrane conductance is of the same order as the contribution of the lipophilic anion.

Membranes with a free hemispherand and a most probably covalently bound hemispherand ionophore, **R3** and **R4** respectively, have about the same resistance as membrane **R2**. However, at the low frequency part of the impedance spectra, a distortion of the spectrum is visible (figure not shown). Such (second order) effects are probably caused by the high amplitude (0.5 V) of the signal. As these effects are not observed with the valinomycin based membranes, the kinetics of the ion exchange of the hemispherand based membranes are probably different from the valinomycin based membranes. Because of these problems the hemispherand containing membranes could not be studied in more detail. Membranes with a lower resistance are probably more suitable for such a study.

The copolymer membrane **C1**, containing valinomycin and KB(ϕ Cl)₄ is crosslinked via a condensation reaction with the Siloprene crosslinking agent K-11. The membrane resistance showed a remarkably low value, 10–20 times lower than the resistance of membrane **R2**, crosslinked via the methacrylate groups. When exposed to the same electrolyte, the dielectric constant of membrane **C1** is lower than the dielectric constant of **R2**. This indicates that although the amount of charge carriers is lower, the membrane conductance is enhanced. Several explanations for this effect are possible. Firstly, due to the formation of a less rigid (micro)structure of the silicone rubber, the resulting mobility of the charge carriers is higher. Secondly, the presence of certain components in the crosslinking agent (e.g. the tin based catalyst) are beneficial for the membrane conductivity because

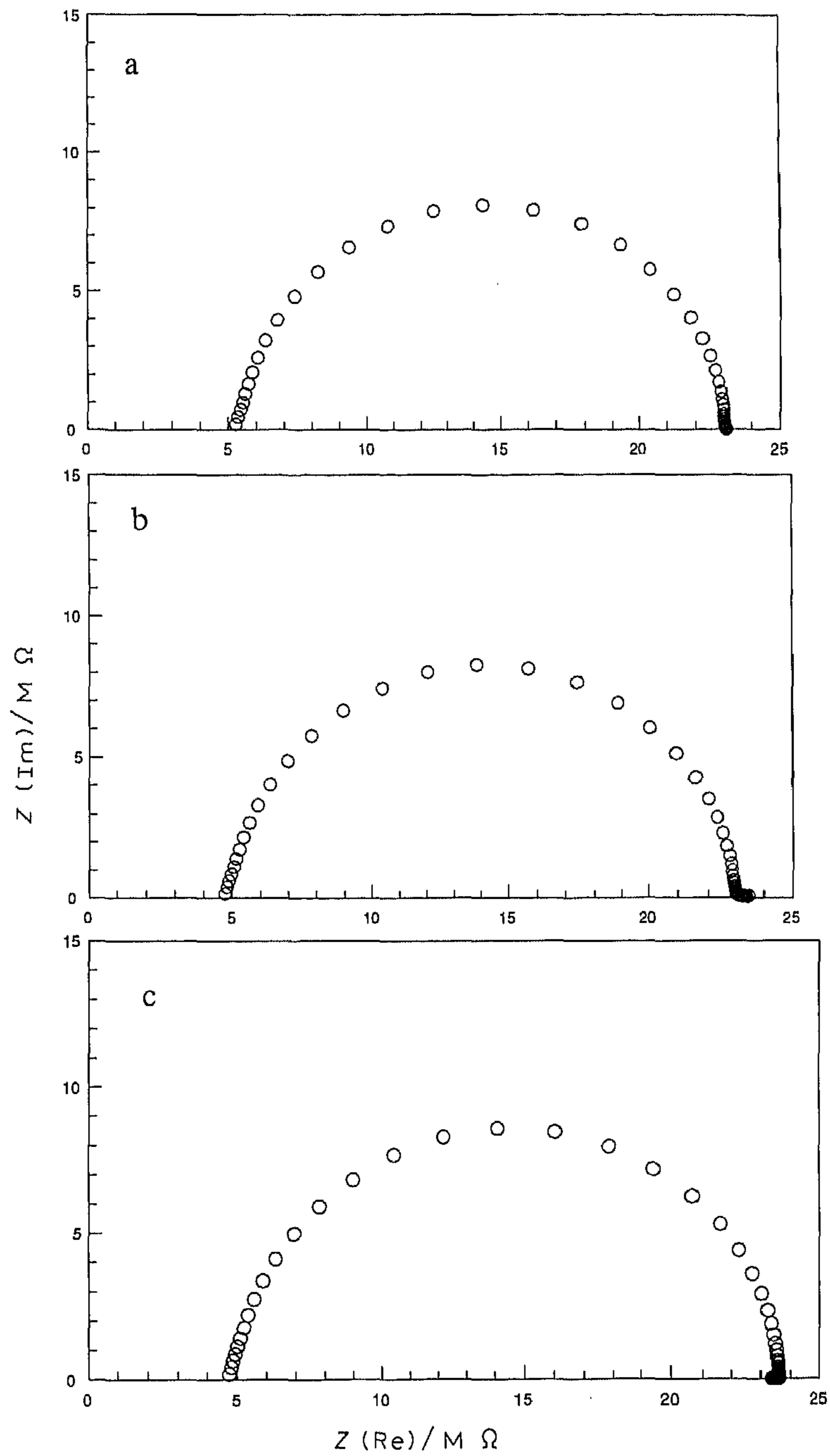


Fig. 2. Impedance spectra of membrane **R2**, conditioned in 0.1 M KCl (a), conditioned in 0.1 M KCl, directly after immersion in 0.1 M NaCl (b), conditioned in 0.1 M NaCl, directly after immersion in 0.1 M KCl (c).

these components have a higher mobility. Thirdly, the crosslinking agent K-11 can give a contribution to the conductance of the crystallite phase present in the membranes. This effect corresponds to a disturbance of the membrane resulting in a shorter electrical path through the silicone rubber phase than the value actually measured for the membrane thickness. Although further research is necessary, the third explanation seems the most plausible, because the measured effect would suggest a very large mobility difference between ions in the different membranes.

The effect of the modification of the polydimethylsiloxane can be illustrated by comparing the resistance of membrane C1 with the resistance of the Siloprene membrane C2. The copolymer has a membrane resistance which is 10–20 times smaller than the Siloprene membrane. The higher conductivity of the copolymer C1 is combined with a higher dielectric constant of the material, which indicates that the number of charge carriers is higher.

Low frequency characteristics of valinomycin containing membranes

The membranes containing valinomycin show interesting behavior of the membrane resistance when they are subsequently exposed to NaCl and KCl solutions. The impedance spectrum of a membrane conditioned in a KCl solution changes from an ideal semicircle (see Fig. 2a) into a flattened semicircle with some tailing in the low frequency part when the membrane is exposed to an NaCl solution (see Fig. 2b). The flat semicircle might indicate an extra resistance term, resulting in a second semicircle partly hidden underneath the first semicircle. However, when subsequent measurements were compared it was observed that the flattened semicircle with the tailing grows to a larger semicircle with almost no tailing. This indicates that the membrane resistance grows larger when the electrolyte is changed from a KCl solution to an NaCl solution. The tailing in the low frequency part of the spectrum is most likely caused by the fact that the resistance changes during the measurement. When a membrane, conditioned in an NaCl solution is exposed to a KCl solution, the impedance spectrum shows a semicircle with some tailing in the low frequency part towards a lower resistance (see Fig. 2c).

It was observed that the change of the impedance spectrum was less pronounced when the conditioned membrane is exposed to low concentrations (10^{-3} – 10^{-4} M) of the new electrolyte, compared with exposure to 0.1 M concentrations. Obviously, the ion exchange is faster when the membrane is exposed to solutions of high concentration.

If it is assumed that the (Na val)⁺ complex is the predominant cation, the higher resistance of membranes exposed to NaCl solutions compared to membranes exposed to KCl can be explained by the lower mobility of the (Na val)⁺ complex compared with the (K val)⁺ complex. This effect has also been observed for plasticized PVC membranes containing valinomycin [17]. In the crystal structure of the (K val)⁺ complex the ion is at the centre of the valinomycin cavity, while in the (Na val)⁺ complex the ion is on the outside [18] thus giving a more hydrophilic structure with lower mobility. It was observed that when the membrane resistance became larger, the membrane dielectric constant also increased when

the membranes conditioned in KCl, are exposed to NaCl solutions. This is probably due to a lesser degree of ion-pair formation of $(\text{Na val})^+$ and $\text{B}(\phi\text{Cl})_4^-$ compared with $(\text{K val})^+$ and $\text{B}(\phi\text{Cl})_4^-$. It has been reported in the literature that the sodium complex has a higher degree of dissociation than the potassium complex when incorporated in plasticized PVC membranes [19]. Although the higher degree of dissociation of Na^+ salts seems contradictory with the higher membrane resistance it can be explained by a larger decrease of the mobility of the complex compared with the increasing dissociation of the Na^+ salts.

Mixed solution experiments

The influence of the membrane selectivity on the resistance behavior could be demonstrated in a series of experiments with mixed electrolyte solutions. In a typical experiment membrane C1 was exposed to a mixture of sodium and potassium chloride. The sodium chloride concentration was maintained at 0.1 M, while the potassium chloride concentration was varied from 0.1 M to 10^{-6} M. In Fig. 3 the impedance spectra of these experiments are given.

The impedance spectra show almost no difference when the potassium concentration is lowered from 0.1 to 10^{-4} M (Fig. 3a,b). When the concentration is further lowered to 10^{-5} M in the low frequency part a small change can be observed (Fig. 3c). Repeated measurements at the same concentration however, show no further change of the spectrum. Obviously at this concentration the ion exchange reaches a turning point. When the potassium concentration is lowered to 10^{-6} M the spectrum clearly changes further (Fig. 3d). Repeated measurements at this concentration show a development of the spectrum towards the spectrum given in Fig. 3e which was measured after 24 h of exposure. At this stage the potassium concentration is enhanced while maintaining the sodium concentration at 0.1 M. In this series of experiments the spectrum clearly changes when the potassium concentration is enhanced from 10^{-5} M to 10^{-4} M (Fig. 3g).

These experiments show that the potassium/sodium ion exchange starts when the concentration ratio is of the same order as the selectivity coefficient ($\log K_{\text{K}^+/\text{Na}^+} = -4.0$ in Siloprene [1]).

Surface layer

Siloprene membranes have also been investigated by Lindner et al. [12] using ac-impedance and activity-step response time measurements. One of the conclusions from this study was that a high resistance surface film was present which caused a second semicircle in the impedance spectrum. This layer could be removed by rinsing with methylene chloride or simply by wiping the surface with a tissue. In the impedance spectrum of the Siloprene membrane C2 a second semicircle at the low frequency side of the spectrum was observed (not shown here). When the membrane was exposed to NaCl solutions the second semicircle was clearly visible, whereas in KCl solutions it was substantially reduced. This second semicircle is most likely related to the observation, described below that the Siloprene K-1000 containing membranes exude small droplets. With the other

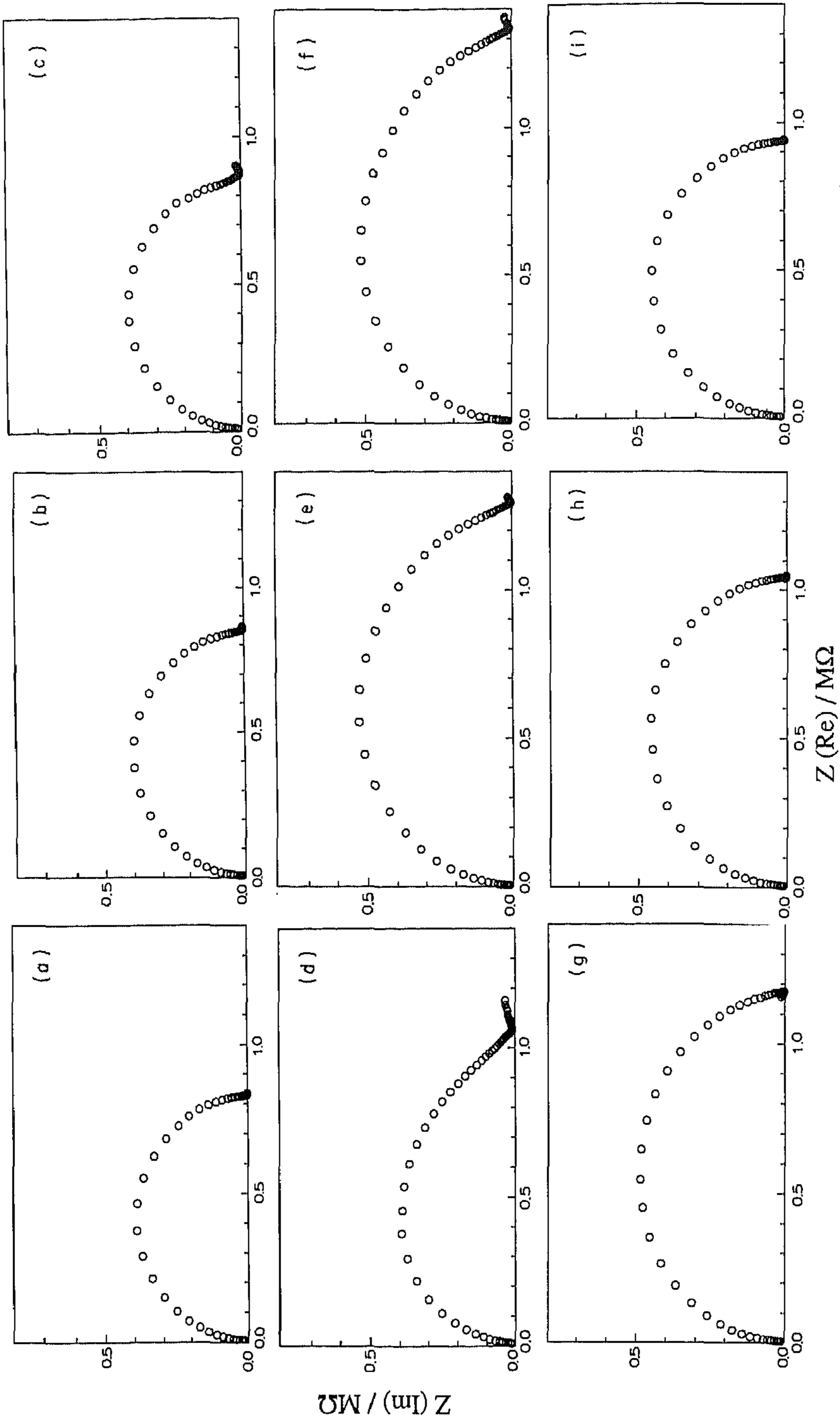


Fig. 3. Influence of the Na^+/K^+ ratio on impedance spectra of membrane C1. The Na^+ concentration is 0.1 M for all spectra, the K^+ concentration is 0.1 M (a), 10^{-4} M (b), 10^{-5} M (c), 10^{-6} M (d), directly after immersion (e), 10^{-6} M, after 24 h of immersion (f), 10^{-5} M (g), 10^{-4} M (h), and 0.1 M (i).

membranes, crosslinked either via the condensation reaction or via the radical reaction, no exudation of droplets was observed and no second semicircle was visible in the impedance spectrum. Smearing the membrane **R2** with a mixture of Siloprene K-1000 with 0.5 wt.% of valinomycin also resulted in a second semicircle in the impedance spectrum. This second semicircle was much larger than for the Siloprene membrane **C2** and was also clearly visible when the membrane was conditioned in KCl solutions. However, it showed the same increase of the resistance when the solution was changed to NaCl as the other valinomycin containing membranes.

Surface study of membranes

Exudation of droplets

The membranes were inspected visually with an optical microscope equipped with Nomarski interference contrast. It was noticed that, a few hours after the solvent casting of the Siloprene membranes, small droplets were present on the surface. The amounts of exuded material increased noticeably in the first two weeks after the solvent casting. After two to three months it was noticed that the droplets had evaporated. Wiping of the surface with methylene chloride at this stage resulted in a clean surface on which the imprint of the droplets was still visible. The droplets only appeared with the membranes containing Siloprene K-1000 (two different batches were tested); on membranes made from the copolymer, crosslinked either via the condensation reaction or the radical reaction, no droplets were observed. From these observations it was concluded that Siloprene K-1000 contains an unknown compound that is exuded after the curing reaction. From the literature it is known that the synthesis of polysiloxanes is an equilibrium reaction between linear and cyclic species [20]. The observed droplets might be these cyclic species.

Valinomycin crystallization

A similar observation experiment was performed on the crystallization behavior of valinomycin in Siloprene membranes (in the absence of $\text{KB}(\phi\text{Cl})_4$). In membranes containing 3 wt.% of valinomycin, needle shaped crystallites could be seen a few hours after the casting of the membrane, and in a few days crystals covered almost the whole surface. Membranes containing 1 wt.% were more suitable for examination of the crystal growth, for they showed a much slower growing rate. Obviously crystallization nuclei must be present before crystallization can begin, for in some membranes one night after the solvent casting, the first crystals were observed and in other membranes crystals appeared only after more than a week. The total crystallization process takes three weeks or more. It was observed that the crystallites grow out of the membrane surface.

In Fig. 4 a picture is shown of the Siloprene surface with valinomycin crystals grown at the surface, also droplets exuded by the membrane are visible. Siloprene membranes and the copolymer membranes with at least 0.48 wt.% of valinomycin

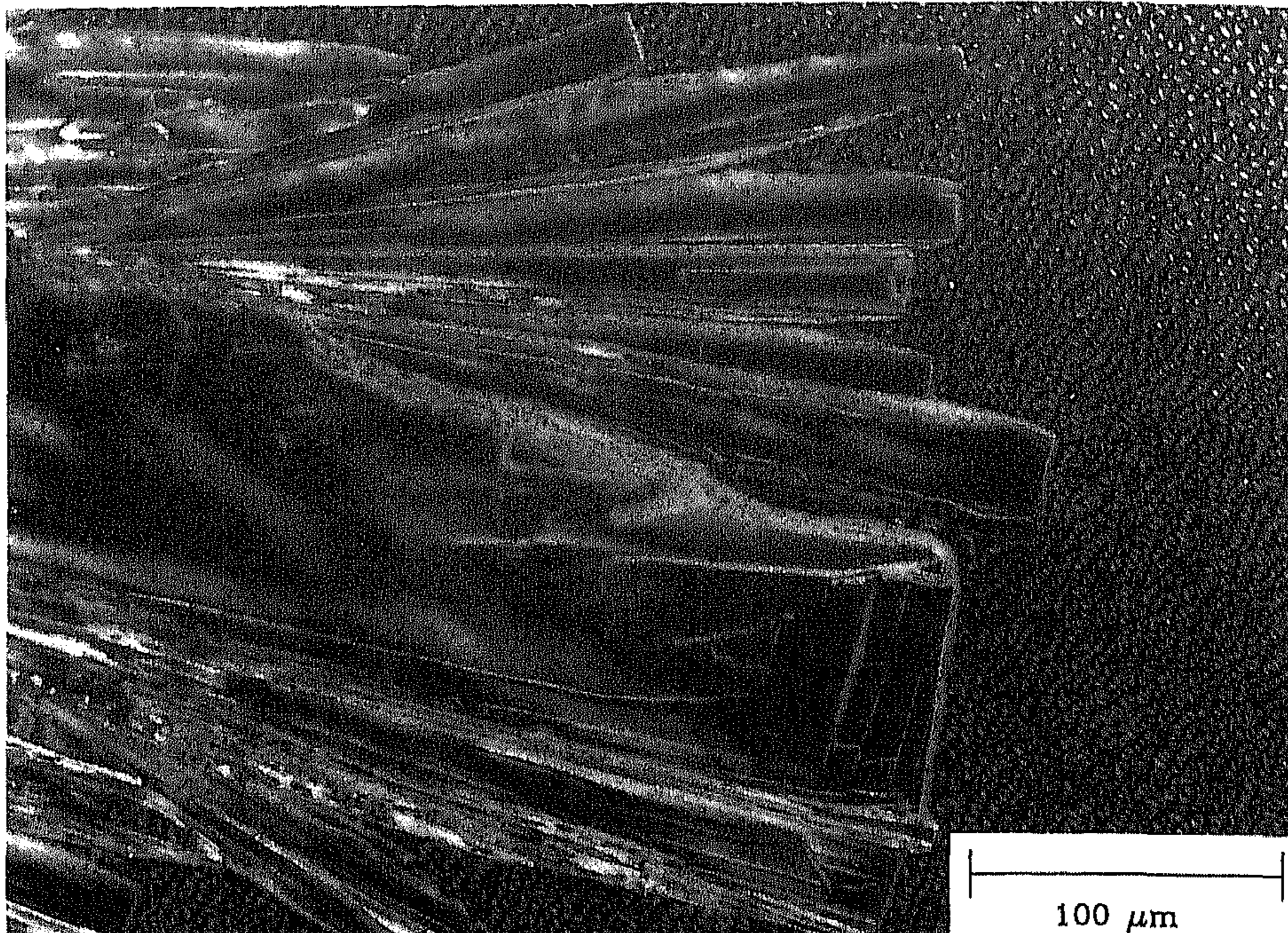


Fig. 4. Valinomycin crystals and exuded droplets on Siloprene surface.

from which 50–70 mol% was present as the complex with $\text{KB}(\phi\text{Cl})_4$ became slightly cloudy a few hours after the solvent casting. The crystallites were clearly much smaller than in the former experiments, thus indicating that the presence of $\text{KB}(\phi\text{Cl})_4$ acts as crystallization nuclei. In these membranes it was observed that the smaller crystallites were mostly present inside the membrane.

PVC membranes, plasticized with DOS (ratio DOS : PVC = 2 : 1) and containing 1 wt.% valinomycin without a lipophilic salt seemed to remain clear, even after several months. It was noticed however, that membranes, damaged by pressing with a pair of tweezers also showed a similar crystallization behavior as the silicone rubber membranes. In these cases the crystallization starts in the damaged area and the crystals also grow into the undamaged areas in long needles. It was noticed that the crystallites grow out of the membrane, similar to the crystallites in silicone rubber. This observation indicates that these plasticized PVC membranes are supersaturated solutions of valinomycin.

It was noticed that undamaged membranes, after immersion in water slowly became cloudy. This process was visible a few hours after immersion, though it took over two weeks for the membrane appearance to stabilise. Microscopic inspection of these membranes, still immersed in water, showed the presence of small ($< 1 \mu\text{m}$) inhomogeneous regions at the surface, these regions were not clearly visible. Inside the membrane however, large inhomogeneous regions were

clearly visible. These regions had diameters up to 100 μm . Membranes without ionophores also showed these regions. This indicates the notorious impurity of PVC.

CONCLUSIONS

Unfortunately the hemispherand containing membranes could not be studied in great detail, due to distortion of the impedance spectra.

The lower resistance of the copolymer membrane crosslinked via the condensation reaction compared with the membrane crosslinked via a radical reaction, is not yet well understood. A possible explanation is a higher conductivity of the crystal phase in the membrane. It is however an interesting observation that can lead to further improvement of the polysiloxane based sensors.

The K^+/Na^+ selectivity of the silicone membranes containing valinomycin could be related to the bulk resistance behavior. Membranes exposed to NaCl solutions showed a higher membrane resistance than membranes exposed to KCl solutions. In a mixed solution experiment the resistance of membranes conditioned in KCl solutions changes only when the K^+/Na^+ ratio is lowered to a value that approaches the selectivity ratio. This indicates that at this point the K^+/Na^+ ion exchange starts.

Microscopic inspection of the membrane surfaces shows the exudation of small droplets from the Siloprene K-1000 containing membranes. The high resistance surface film on Siloprene membranes, first reported by Lindner et al. [11] and confirmed here by the impedance method is likely to be related to the exudation of these droplets. The siloxane copolymer, crosslinked either via a radical or a condensation reaction seems to be free of such a surface film. If this conclusion is correct we now have the availability of a membrane material with which it is possible to study the real interfacial properties without the interference of a surface film.

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