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Electrochemical characterization of composite membranes based on crown-ethers intercalated into montmorillonite

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Abstract: Oxyethylene macrocyclic compounds (crown-ethers) act as ligands of intracrystalline cations of certain layered silicates as montmorillonites. Stable intercalation materials are formed which are used to prepare organic-inorganic membranes by encapsulating these intercalation compounds with a polybutadiene thin coating. Electrochemical Impedance Spectroscopy (EIS) is used to study the resulting composite membranes in contact with aqueous electrolytes. From the impedance plots, the ionic resistance of the membranes is obtained. The thickness of the polybutadiene coating is an important factor determining the ability of ions to pass across the membrane. Marked differences in the ionic resistance are observed as a function of the nature of the interlayer macrocyclic compound. For non-intercalated montmorillonite membranes, the ionic resistance is strongly reduced, whereas for some crown-ether intercalated materials such as 18-crown-6 and dibenzo 24-crown-8, iono-selective membranes are obtained. Concerning the nature of the electrolyte, cations exhibiting greater hydration energies show higher difficulties to pass through the membrane and, consequently, the ionic resistance increases.

Key words: Membranes – impedance – crown-ethers – montmorillonite – ion-conductivity

Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful technique for studying electrical and electrochemical properties of a large variety of systems [1]. Concerning the use of EIS to study membranes, both bulk and interfacial properties of these systems can be determined. In this way, Armstrong et al. [2–4] have applied the impedance measurements to characterize PVC membranes containing complexing agents of alkaline salts, as valinomycine and some crown-ethers, which can act as neutral carriers for cations in the membrane. The alkaline ion is complexed by the valinomycine or by the crown-ether. Thus, the cation is transported through the membrane in the cavity of the complexing ligand which acts as a carrier. Armstrong et al. also introduced relatively immobile anions in those membranes such as tetraphenylborate, in order to improve the membrane behavior [2]. This presupposes that the membrane behaved like a viscous liquid of low dielectric constant.

Although these membranes function very well, there are some specific applications where the use of alternative membrane materials offers distinct advantages [5]. In this way the 2:1 clay minerals, such as montmorillonite, can be used to prepare new membrane materials. In contact with aqueous electrolytes, the montmorillonite acts as a cation-exchanger and also has the ability to remain in a colloidal state that could facilitate the transport mechanism proposed by Armstrong et al. [2–4]. Certain oxyethylene compounds (crown-ethers and cryptands) are intercalated into homoionic montmorillonites and act as ligands of interlayer cations (Fig. 1). Stable intercalation compounds are formed [6–9]. We have taken advantage of this behavior to prepare organic-inorganic membranes based on treating Na-montmorillonite and different crown-ethers. The electrochemical behavior of these materials in contact with different aqueous salt solutions was studied by impedance spectroscopy.

Experimental

Materials and products

Montmorillonite from Upton (Wyoming, USA) was supplied by Ward's Natural Science Establishment, Inc. Homoionic Na-montmorillonite has been prepared by treating the $< 2\ \mu m$ diameter fraction with 1 M NaCl solution. Cation exchange capacity: 0.91 meq/g.

The 18-crown-6 (18C6) and the dibenzo-24-crown-8 (DB24C8) crown-ether were commercial products supplied by Aldrich. The crown-ethers were dissolved in methanol (Carlo Erba, RPE-ACS grade) (dried over 3 Å molecular sieve) and intercalated as described previously [6–7]. Polybutadiene (PB) containing 45% (w/w) of vinyl groups and 55% (w/w) of a mixture of the *cis*- and *trans*-1,4 conformations, average M.W 4,500 Dalton (Aldrichs) was dissolved in toluene and used as coating material.

C222 criptand used for complexing NaCl in aqueous solution was supplied by Merck.

Membrane preparation

Self-supporting films of crown-ether/Na-montmorillonite were prepared and characterized as described previously [6–7]. The intercalation process of 18C6 and DB24C8 is schematized in Fig. 1.

By spin coating a polybutadiene layer was deposited on each face of these films. A certain number of drops of polybutadiene/toluene solutions (5, 15 and 25% in weight) were added on the top of films of Na-montmorillonite or of the intercalation compounds (30–40 μm thickness and 7 cm^2 surface area) while it was spinning. Variations in the concentration of the polybutadiene solution allowed to produce coatings of different thickness. Heating to 180 °C for 3 h accelerated the coating process. This procedure led to a good adherence between the organic coating and the montmorillonite surface. Membranes were obtained with a uniform coating thickness (1 to 5 μm on each side).

Membrane characterization

Intercalation materials were characterized by different techniques (elemental microanalysis, XRD, IR, LMMS and ^{23}Na NMR spectroscopies, TGA, DTG and DTA analysis, and adsorption microcalorimetry) as reported elsewhere [7–9]. Scanning electronic microscopy, SEM, (Cambridge Stereoscar 100, 10KV) and laser scanning microscopy, LSM, (Confocal Zeiss Microscope) were used to determine the homogeneity, morphology and thickness of the polybutadiene coatings.

Electrochemical characterization of the membranes was performed by impedance spectroscopy adopting a four electrode configuration. The membranes were placed in the middle of a typical Hittorf cell [2]. On both sides of the membranes the chambers are filled up with identical volume of electrolytic solution at the same concentration. A Solartron 1255 frequency response analyzer coupled to a PAR 273A potentiostat was used for the impedance measurements. The measurement was conducted by superimposing an ac voltage of 10 mV amplitude close to the membrane potential, and the frequency ranged from 10 mHz to 100 KHz. Finally, the impedance data were fitted using the immitance software package "EQUIVCRT" of Boukamp [10].

Results and discussion

Membrane design

Films of Na-montmorillonite and of their crown-ether intercalation derivatives are composed of aggregates of microcrystalline particles (Photomicrograph 1) which present low mechanical resistance. The rapid absorption of water produces a fast swelling of the Na-montmorillonite and, in general, all these materials broke when brought into contact with electrolytic solutions for a certain period of time, mainly with diluted solutions. In order to improve the mechanical resistance of these systems, we initially proceeded to compact them by a pressure of 700 MPa. This

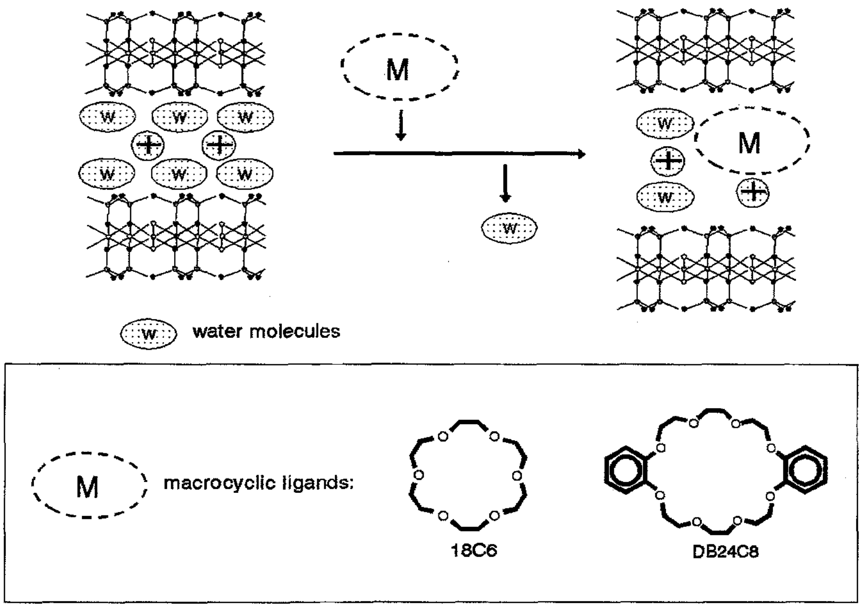
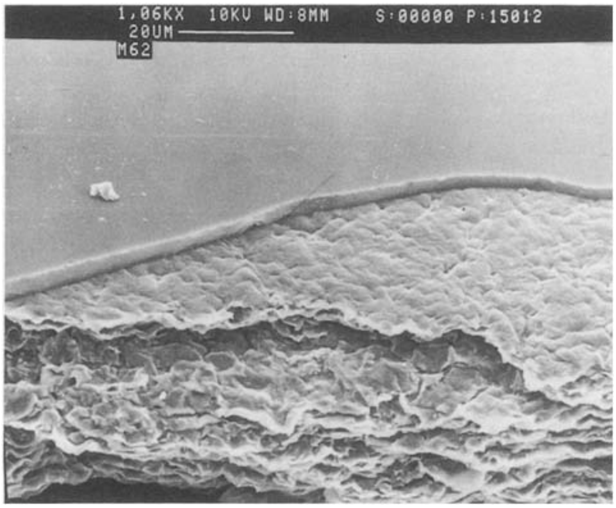


Fig. 1. Schematic model representing the intercalation of 18-crown-6 (18C6) and dibenzo-24-crown-8 (DB24C8) into montmorillonite



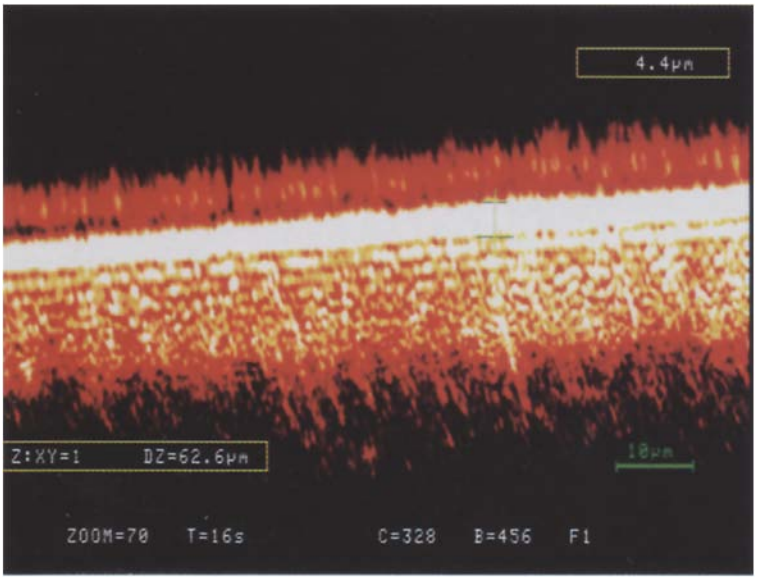
Photomicrograph 1. SEM image of a Na-montmorillonite/18C6 film coated by a PB layer of 5 μm thickness

operation achieved a partial improvement and, in a few hours, the material exposed to the electrolytes underwent a degradation unacceptable for membrane applications.

Operative membranes based on the montmorillonite intercalation compounds are obtained by a polybutadiene coating of both faces of clay films. The SEM (Photomicrograph 1) shows the cross-section of such a composite membrane based on 18C6/Na-montmorillonite. The stacked laminar aggregates are relatively well arranged along the (a, b) lattice plane of the silicate, although there are clear discontinuities and micro-channels between particles through which the electrolyte can pass freely. Photomicrograph 2 was obtained by the LMS technique, showing a cross-section of the membrane, again illustrating the uniformity (white zone) of the polybutadiene coating on one of the membrane faces.

Impedance spectroscopy

The Nyquist representation of the impedance data of the membranes usually shows two arcs (Fig. 2). These results are interpreted with the aid of an equivalent circuit [1] inserted in Fig. 2. The high frequency arc is usually attributed to the membrane itself [2, 11]. The interpretation of the low frequency arc is unclear. This arc has been related sometimes to the charge-transfer reaction at the electrolyte/membrane interface [2], and on other occasions to diffusion of electroactive species through the membrane [12]. When the diffusion layer has a finite thickness, an arc appears at low frequencies in the Nyquist plot. Since the experimental data are scattering, this arc may be confused with a semicircle, and the diffusion process ascribed to this arc can be confused with the



Photomicrograph 2. LSM image of the cross-section of a PB[Na-montm/18C6]PB composite membrane

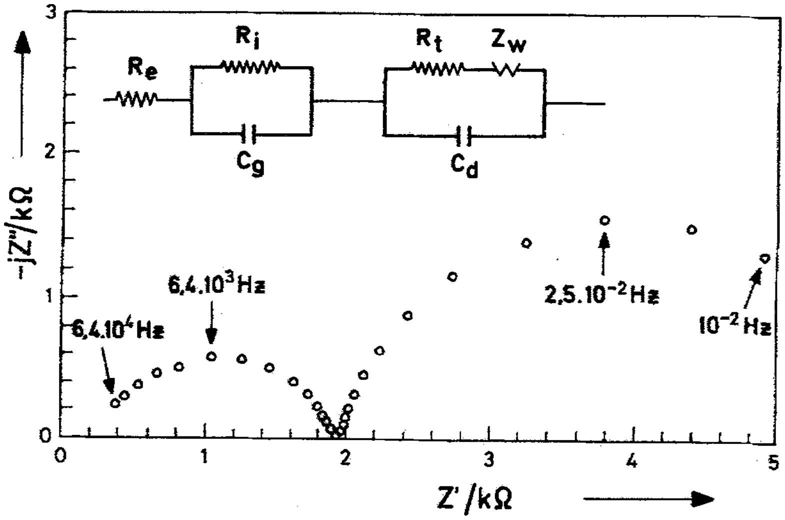


Fig. 2. Representative Nyquist plot of a PB[Na-montmorillonite/crown-ether] PB composite membrane in contact with an electrolytic solution. Inserted is the corresponding equivalent circuit. The crown ether is DB24C8 and the electrolyte is a NaCl 0.01 M solution

typical semicircle associated to a charge transfer process. In the proposed equivalent circuit, R_e represents the electrolyte resistance, R_i usually is related to the ionic resistance of the membrane, C_g is assigned to the geometric capacitance of the membrane, C_d is the double layer capacitance, R_t is the charge-transfer resistance, and Z_w the Warburg diffusion impedance [13].

According to this model, the impedance diagrams might show two semicircles and a diffusion tail. Theoretically also one semicircle is allowed to appear. This can occur when the two time constants $\tau_1 = C_g R_i$ and $\tau_2 = C_d R_t$ acquire relatively close values, and the corresponding semicircles overlap to a single arc. It may also happen that the charge transfer process will be very fast, and the R_t values will tend to zero. In such a case, also one semicircle appears in the Nyquist plot.

In the Nyquist plot of our membranes (Fig. 2), the low frequency arc could be also interpreted as a curved diffusion tail, because the high values of capacitance (pseudocapacitance) are derived from the expression:

$$C = 1/\omega_{\max} R \ .$$

This conception is also supported by the fact that the Warburg coefficient (σ_w) calculated from the following equation:

$$\sigma_w = 1.063 Z''_{\max} \cdot \sqrt{\omega_{\max}} \ ,$$

where $Z''_{\max}$, $\omega_{\max}$ and R are the imaginary component of the diffusion impedance, the frequency at the top of the low-frequency arc, and the resistance value of the possible resistor associated to this arc [14], adopts values (Table 1) of the same magnitude orders as those found by Coving in PVC membranes [11].

Physical meaning of parameters obtained from the Nyquist plots.

The ionic resistance

Only when R_t is zero is the value of R_i determined with accuracy. This value is equivalent in value to the diameter of the high frequency semicircle, and it is affected by i) the ionic resistance of the narrowest conduction channels of the membrane and ii) the ionic resistance of the electrolyte in the macroporous perforations that may be formed in the membrane with proceeding exposition time. The value of R_i may be inversely proportional to the average cross-section (S) of the conduction channels and directly proportional to the length (l) of these channels. For this reason, the ionic resistance changes with time during the time when membrane is impregnated with electrolyte and undergoes certain geometric changes.

The ionic resistance of the membrane depends not only on the intrinsic nature of its bulk material, but also on the nature of the electrolyte which it is in contact with. The thickness of polybutadiene coating is also an important factor which directly influences the ability of the ions to pass through the membrane. There is a drastic difference in the conductivity of the composite membranes compared to films of pure polybutadiene of similar thickness. Thus, for 2 to 10 μm thickness of polybutadiene coatings (1 to 5 μm each side) on a film of 18C6/montmorillonite, R_i is between 10^3 and 10^4 Ω, whereas for pure polybutadiene films of the same thickness it is between 10^7 and 10^{11} Ω [15].

Table 1. Pseudocapacitance (C) and Warburg coefficient (σ_W) (obtained from the maximum of the low frequency arc). Membrane: PB[Na-montmorillonite/DB24C8]PB

Electrolyte	C (F) × 10^{-3}	σ_W ($\Omega \cdot s^{-1/2}$)
NaCl 0.5 M	1.78	670
NaCl 0.1 M	1.66	665
NaCl 0.05 M	0.91	919
NaCl 0.01 M	4.97	434
NaCl 0.001 M	1.66	1213

The high ionic permeability of the polybutadiene films is caused by the liberation of solvents during the preparation of the membrane. Initially, the solvent is absorbed by the Na-montmorillonite or by its intercalation products, and, later on it is desorbed when the material is heated. This process should affect the texture of the polybutadiene coating, so that it is quite different from its usual form when it is deposited on non-microporous surfaces.

The thickness of the polymer coating also affects a very important membrane property: the stabilization time. This parameter is deduced from the plateau of R_i attained during the contact of the membrane with the electrolyte solution. The kinetics of this process indicate a sudden initial decrease of R_i. In order to prevent the correct determination of the R_i, the impedance measurements were made several hours after contacting the membrane with the electrolyte, so that the initial and imprecisely measured values are excluded.

Figure 3, for example, illustrates the kinetics of the stabilization of process of a membrane of the type PB[Na-montmorillonite/18C6]PB in contact with a 0.01 M NaCl. Under the condition that R_i is invariable in time, the change of the ionic resistance with the concentration of the electrolyte (NaCl) is reversible (Fig. 4); the hysteresis is minimal, indicating that the membrane is quickly recovered.

The influence of the nature of the electrolyte, which is of great interest for ionic selectivity, is shown in Fig. 5. The transport through the membrane is more hindered (higher values of R_i) for the more voluminous ions.

The passage of the ions should be limited essentially by the microporous texture ascribed to the polybutadiene coating ("ionic sieve" effect). This

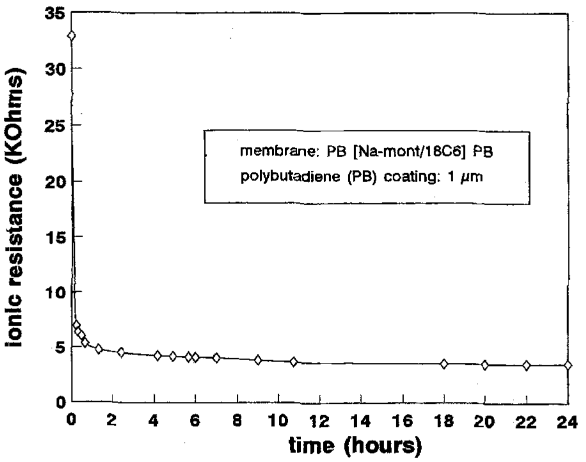


Fig. 3. Time dependence of the ionic resistance stabilization (R_i) of PB[Na-montm/18C6]PB composite membranes. PB thickness: 1 μm. Electrolyte: NaCl 0.01 M

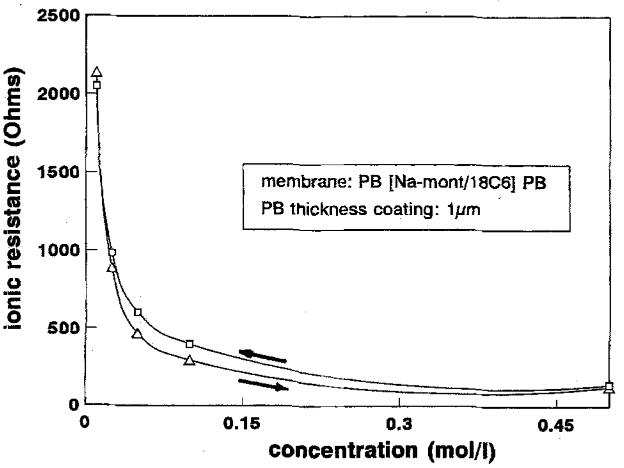


Fig. 4. Reversibility of the ionic resistance (R_i) as a function of the NaCl concentration

effect is clearly highlighted when increasing amounts of C222, a strong complexing agent, are added to a PB[Na-montmorillonite/18C6]PB membrane in contact with a 0.01 M solution of NaCl (Fig. 6). The ionic resistance of the membrane increases considerably until a plateau is reached when the amount added is slightly above the value necessary to complex all the ions in solution. The C222/NaCl complex in an aqueous medium is extremely stable ($-\Delta H = 31.88$ KJ/mol; $\log K = 3.9$) [16] so that all Na^+ ions

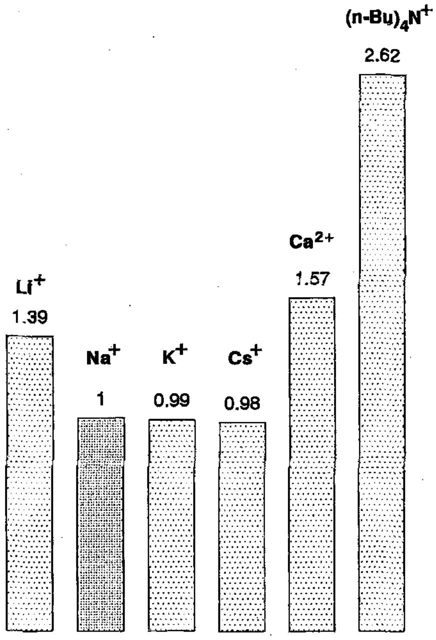


Fig. 5. Relative ionic resistance (R_i) of PB[Na-montm/18C6]PB composite membranes (PB thickness: 1 μm) in the presence of different 0.01 M electrolytes

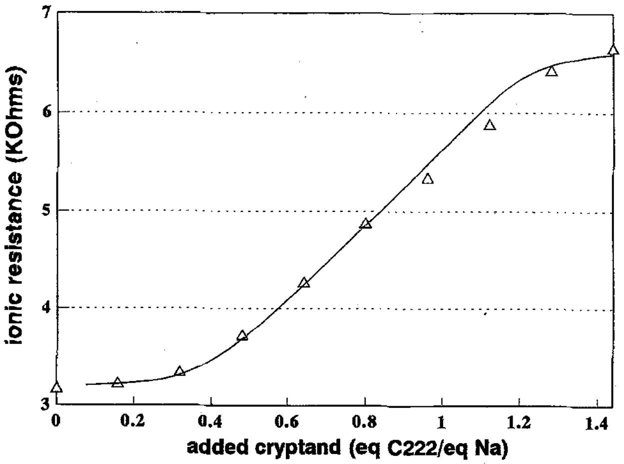


Fig. 6. Ionic resistance (R_i) of PB[Na-montm/18C6]PB composite membranes as a function of the amount of cryptand C222 added to the electrolyte. PB thickness: 1 μm. Electrolyte: NaCl 0.01 M

may be admitted to be encrypted in the macrobicyclic cavity, forming a voluminous macrocation, which is sterically hindered from diffusing through the membrane. The resistance increase is not due to changes in the conductivity of the electrolytic solution after the addition of the cryptand, as the value of R_e scarcely varies (912 Ω in the NaCl solution; 966 Ω in the same solution containing the cryptand).

The membrane does not have a notable selectivity towards the alkaline ions with the exception of Li^+ ions (Fig. 5). The difficulty of transporting Li^+ through the pure polybutadiene is related to the high hydration energy of this cation [15]. The difference still increases with the polybutadiene coating thickness and a behavior similar to that of pure polybutadiene is attained. Figure 7 shows the variation of the ionic resistance of the PB[Na-montmorillonite/18C6]PB membranes (the thickness of each polybutadiene coating is 5 μm) with the contact time for 0.5 M solutions of Li^+, Na^+ and K^+ chlorides. The membranes reach stable R_i values which follow the sequence:

$$R_i(Li^+) > R_i(Na^+) \sim R_i(K^+) \sim R_i(Cs^+) .$$

A membrane that has been exposed to the LiCl solution over several days (stabilized ionic resistance of around 2650 Ω) shows $R_i = 2040$ Ω if LiCl is replaced by NaCl solution of the same concentration within a few minutes. If the NaCl solution is again replaced by LiCl solution the membrane recovers to the initial value of ionic resistance within 20 min.

The membrane capacitance

The membrane capacitance (C_g) is calculated at the maximum of the high frequency semicircle, according to the equation

$$C_g = 1/\omega_{max} \cdot R_i .$$

The value of C_g depends on both the chemical and physical nature of the membrane, particularly its thickness, chemical composition and microscopic structure. The values of C_g of the different composite membranes are between 10^{-9} and 10^{-8} F. These values are much higher than those of a free polybutadiene film (10^{-12} F, [15]) and of dehydrated Na-montmorillonite (10^{-11} F). The high capacitance is attributed to the high absorption of water in the membrane [17]. It should be pointed out that C_g of the composite membranes remains invariable with time, in contrast to other membranes, especially pure polybutadiene [15]. Probably, the membrane absorbs a high amount of water in the first stages of exposition to the electrolyte and the C_g values increase quickly with time. The problem is that these values cannot be determined until the membrane reaches the stabilization conditions, i.e., when C_g does not change with time.

C_g decreases with increasing thickness of the polybutadiene coating. In a membrane containing Na-montmorillonite/18C6, for example, C_g decrease from $5 \cdot 10^{-8}$ to $2 \cdot 10^{-9}$ F for coatings of 1 μm to 12 μm. This indicates that the polymer content has the greatest influence over the dielectric properties of the membrane. Nevertheless, there are some differences in the value of C_g, related to the type of the intercalated oxyethylenic compound. The highest values of C_g (Table 2) are found for macrocyclic compounds with the largest enthalpy of formation of the intercalation complex. The complexation between the oxyethylenic

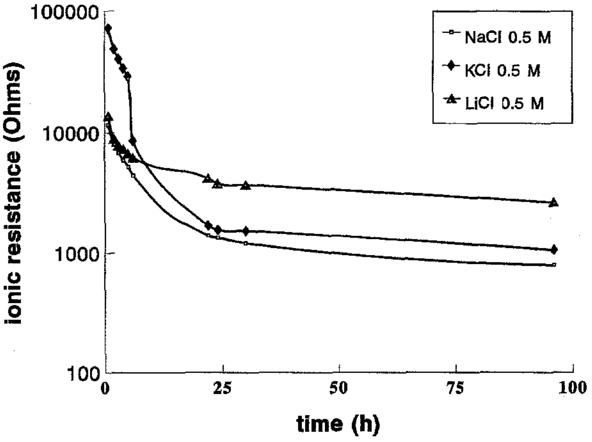


Fig. 7. Time dependence of the ionic resistance (R_i) of PB[Na-montm/18C6]PB composite membranes for 0.5 M solutions of different salts. PB thickness: 5 μm

Table 2. Capacitance (C_g) of PB[Na-montmorillonite/crown-ether]PB (1 μm polybutadiene (PB) coating) placed in contact with a NaCl 0.5 M solution, the Na-montmorillonite film was measured in absence of any electrolyte

Membrane	C_g (F)
Na-montmorillonite	–
Na-montm/18C6	$5.5 \cdot 10^{-8}$
Na-montm/DB24C8	$1.5 \cdot 10^{-8}$
pure PB film (10 μm)	$1.0 \cdot 10^{-10}$
Na-montmorillonite film measured in dry conditions	$1.0 \cdot 10^{-11}$

ligands and the interlaminar cation (Na^+ in this case) prevents the entry of water molecules into the interlayer space of the phyllosilicate. In membranes based on Na-montmorillonite (non-intercalated), the system behaves like a pure resistance, allowing the electrolyte to pass through practically unimpeded and, thus, the system loses the characteristic property of a membrane.

Transport mechanism through membranes

The initial hypothesis in the design of the membranes was that the crown-ethers may complex the ions in solution, facilitate their transfer between the two interfaces, thus acting as an active component of the membrane. We have shown that the intercalation compound alone does not meet the requirements of a membrane, and that the presence of a polymer support (in this case composed of polybutadiene coatings) is required.

Ideally, the coating should be an inert support, and the intercalation material should regulate the ionic transport through the membrane. However, the preparation of the membrane changes the polybutadiene film in such a way that the ionic permeability increases sharply, perhaps due to the creation of channels on a molecular scale which develop during the evaporation of the solvent. Thus, the ionic selectivity observed may be at least partially explained by a sieve effect. The migration of the electrolyte through the channels of the membrane will follow a diffusion mechanism, which could be included in the basic mechanisms (passive transport) proposed by Strathman [18]. According to this model the polybutadiene coating controls the passage of the electrolyte by the size of the channels created. Taking the passage of sodium chloride between phases 1 and 2 as the reference, the transport of electrolytes with more voluminous ions (hydrated Li^+, tetrabutylammonium) through the membrane (Fig. 5) is retarded.

The mechanism of assisted transport implies the participation of the intercalation composite as an active phase. Considering the large amount of water retained by the membrane, this phase is in a colloidal state, which facilitates its action. Focusing on the example of the Na-montmorillonite/18C6 composite, the crown-ether, which can act as a complexing ion, and even the clay due to its ion-exchanger properties may potentially act as carriers. Both are known to be selective towards the interaction with ions. Thus, the 18C6 cannot form complexes with cations such as tetrabutylammonium and Ca^{2+} and the transport of these ions through the membrane is disfavored, which agrees with the experimental observations.

Although there seem to be arguments for and against both types of mechanism (passive and assisted transport), the predominance of one mechanism cannot be assured. The different value of R_i when the NaCl electrolyte is displaced for $Bu_4N^+Cl^-$, seems to indicate that the sieving effect of the polybutadiene coating is more important. The behavior of the membrane when subjected to the passage of Li^+ ions seems to be linked to the nature of the polybutadiene coating. These results support a greater participation of a passive transport mechanism in these membranes rather than an assisted transport mechanism.

Conclusions

Intercalation of crown-ethers into montmorillonite produces useful materials for the design of organo-inorganic membranes. The polybutadiene coating is necessary to improve the mechanical properties and to control ion permeation. Crown-ethers act as a sensing component in the impedance response of these systems. The ionic resistance is strongly related to the nature and concentration of the electrolyte. Although there seem to be arguments for and against passive and assisted transport mechanism, the predominance of one of them cannot be assured.

Acknowledgements

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