Transport of $\text{Na}_2\text{SO}_4$ and $\text{MgSO}_4$ solutions through a composite membrane

J. Benavente* and G. Jonssonb

*Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga (Spain)

bChemical Engineering Department, Technical University of Denmark, DK-2800 Lyngby (Denmark)

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Abstract

Retention curves with a composite membrane (HR 95) have been measured for different solutions of $\text{Na}_2\text{SO}_4$ and $\text{MgSO}_4$. Salt permeabilities in the skin and the porous layer of the composite membrane have been calculated. The results show that the salt permeability in the skin layer is 15% of that corresponding to the porous layer. Electrical resistances for the composite membrane and another membrane similar to the supported membrane (without skin layer) have been measured using both direct and alternating current. From the a.c. values, assuming that no concentration polarization exists at the skin-porous layer interface, the electrical resistance for the skin layer at different concentrations was estimated. The membrane resistance values were also determined by impedance spectroscopy measurements, and the results agree with those previously found by a.c. measurements.

Keywords composite membranes, reverse osmosis, electrical resistance

Introduction

The transport properties of composite membranes are commonly studied on the basis of a two-layer model by means of the Kedem-Katchalsky equations for the volume and salt fluxes through the whole membrane [1,2]. This model assumes that the membrane consists of two different elements, the skin and the porous layer, coupled in series by an imaginary solution which is in local equilibrium with both elements. One of the problems presented by this model is that all coefficients must be measured for the entire membrane and for one of the layers separately, which is not always possible. On the other hand, as Kedem and Katchalsky pointed out, the relationship between flows and forces in series of membranes shows that for some parameters the rule of additivity does not generally hold. This means that, by reversing the direction of the forces, not only is the direction of the flows reversed, but also a change of their magnitude can be measured. This fact
stems from the different values of the transport parameters in each layer, which also affect the concentration profile in both layers.

In this work, the transport of sulphate solutions across a composite membrane has been studied under different external conditions. Experiments with two kind of gradient across the membrane (pressure and electrical potential gradients) have been carried out in order to determine some characteristic parameters for both skin and porous layers of the composite membrane.

From reverse osmosis measurements, the retention–flux relationships for the composite membrane were obtained for different Na₂SO₄ and MgSO₄ solutions. From these experimental values, the reflection coefficient and the solute permeabilities in the skin and the porous layer were calculated.

The electrical resistances of two membranes, the composite one and another similar to the porous sublayer, were also measured using both direct and alternating current. Differences in the d.c. values of the resistance for the composite membrane, depending on the polarity of the electric current, indicate the different concentration profiles in each sublayer. From the a.c. values of the resistance $R_m$, for both composite and porous membranes, and assuming that no concentration polarization at the skin–porous layer interface exists, the electrical resistance of the skin layer, $R_s$, has been estimated. The variation of $R_m$ and $R_s$ with concentration for Na₂SO₄ and MgSO₄ solutions was also obtained.

A comparison of these results with those previously obtained for chloride electrolytes (NaCl and MgCl₂) indicates that the solute permeability in the skin layer for the sulphate solutions is 50% lower than that found for the chloride ones, which agrees with the higher values obtained for both salt retention and electrical resistance when sulphate solutions are considered.

**Experimental**

**Reverse osmosis measurements**

The reverse osmosis measurements were carried out in the test cell I without sectioning described elsewhere [3]. A composite membrane from Dow Denmark Separation Systems (DDSS HR 95) was used. To avoid compaction effects during the reverse osmosis measurements, the membrane was pressurized at 50 atm for 3 hr before use. The experiments were carried out with Na₂SO₄ and MgSO₄ aqueous solution at (25.0 ± 0.5) °C.

For each electrolyte, two retention curves (retention versus permeate flux) were measured.

(i) skin layer facing the high pressure side.

The pressure ranged from 8 to 50 atm and the concentration of the feed solution from $10^{-3}$ to $4 \times 10^{-1}$ N;

(ii) porous layer facing the high pressure side.

Measurements for three different feed solutions ($5 \times 10^{-3}, 10^{-2}$ and $5 \times 10^{-2}$ N) were carried out. Pressure values ranged from 3 to 9 atm.

Solute concentrations of the feed and product were determined by conductivity measurements using a Radiometer CDM-3 conductivity meter.

**Electrical resistance measurements**

The experimental device for measuring the membrane electrical resistance was previously described [4]. Measurements were carried out with direct and alternating current and with two types of membrane: the HR 95 composite membrane indicated above and a homogeneous polysulfone membrane (PS), which is similar to the porous sublayer of the composite membrane. In all cases, the concentration of the solutions separated by the membranes had the same value. Measurements were carried out with Na₂SO₄ and MgSO₄ solutions with con-
centrations ranging between $2 \times 10^{-3}$ N to $5 \times 10^{-2}$ N.

For d.c. measurements, a procedure similar to that indicated in [5] was followed, with one pair of working (gold) and another of probe (platinum) electrodes placed on either side of the membrane. An automatic precision bridge (Wayne Kerr B905) with four frequencies was used for a.c. measurements. As Nakanishi et al. [6] indicated, some preliminary measurements were performed in order to choose an adequate frequency value, which was 1 kHz. In both cases, the membrane resistances were taken as the difference between the resistances of the cell with and without a membrane [6]. The contributions of the surface-contact resistances are the same for both measurements, and consequently they cancel out.

For both membranes, impedance measurements were also obtained by means of a Frequency Response Analyser (Solartron 1255) for a range of frequencies between 100 Hz and 15 MHz and with 0.2 V as maximum voltage. The impedance measurements were corrected by software, and the influence of the measuring cell, connecting cables and other parasitic capacitances was eliminated.

Results and discussion

Reverse osmosis

In this study, retention-flux relationships with a composite membrane under different external conditions were obtained. The Spiegler–Kedem equations for the local volume and salt fluxes through each layer of a composite membrane are [7]:

\[
J_v = -P_f (dP/dx - \sigma_s d\pi/dx) 
\]

\[
J_s = -P_s d\pi/dx + (1 - \sigma_s) cJ_v 
\]

\[
J_v = -P_f (dP/dx) 
\]

\[
J_s = -P_p d\pi/dx + cJ_v 
\]

where $P_s$, $P_p$, $P_f$, and $P_f$ are the local solute and the specific hydraulic permeabilities for the skin and porous layers respectively, and $\sigma_s$ is the reflection coefficient in the skin layer; however, it was assumed that the reflection coefficient in the porous layer is zero ($\sigma_p = 0$).

Integrating the Spiegler–Kedem equations for the solute flux with the steady state condition, the following relationships among bulk ($C'$), product ($C''$) and intermediate ($C_i$) concentrations were obtained [2] for the two mutually reversed membrane positions shown in Fig. 1:

- skin layer facing the high pressure side (Fig. 1a):
where \( \omega_s \) and \( \omega_p \) are the solute permeabilities in the skin and the porous layer of the composite membrane. These expressions permit us to estimate the characteristic membrane parameters \( \sigma_s \), \( \omega_s \), and \( \omega_p \).

The experimental retention–flux curves when the composite membrane is facing the high pressure side, for different Na\(_2\)SO\(_4\) and MgSO\(_4\) solutions, are drawn in Figs. 2 and 3, respectively. Retention values were corrected for concentration polarization as described in Ref. [3]. In both cases, activity retention was considered \((R_a = C'/C'' / C'' / C''')\) and a decrease of \( R_a \) values with concentration was found [8]. A comparison of these retention values with those found for NaCl and MgCl\(_2\) solutions is also indicated in Figs. 2 and 3 \((C=10^{-2} \text{ N})\). As can be seen from both figures, retention is lower for both chloride electrolytes.

From eqn. (5) the reflection coefficient and solute permeability in the skin layer can be determined for each concentration. Equations (6) and (7) permit the intermediate concentration

![Figure 2](image_url)
and solute permeability in the porous layer to be estimated using a three parameters non-linear fitting procedure. Table 1 shows the average values of $\sigma_s$, $\omega_s$ and $\omega_p$ for the whole interval of concentrations. These results indicate that the specific solute permeability in the skin layer is about 15% of that in the porous layer.

A comparison of these values with those found for NaCl and MgCl$_2$ solutions [5] shows that sulphate solutions have lower specific solute permeability in the skin layer (by ca. 50%), but that the solute permeability in the porous layer is almost independent of the kind of electrolyte considered.

**Electrical resistance**

When direct current was used for electrical resistance measurements, two different values were found, depending on the polarity of the current. We call the resistance obtained $R_m(-)$ when the skin layer is in contact with the cathodic side, and $R_m(+)\) when it is in contact with the anodic one. This asymmetry is more evident at low concentrations, and it has already
been reported for a similar composite membrane with NaCl and MgCl₂ solutions [5]. This finding was attributed to the different transport properties of each sublayer of the composite membrane and the different values attained by the concentration at the skin–porous layer interface under the two opposite current polarities. Variations of the electrical resistance with concentration for both membranes and electrolytes are shown in Figs. 4 and 5. As can be seen from these figures, \( R_m(+) \) and \( R_m(-) \) values hardly differ at high concentrations; also, both \( R_m(-) \) and \( R_m(PS) \) values have a quite similar rate of decrease.
In order to minimize the effect of concentration profiles built up in each sublayer of the composite membrane with direct current, electrical resistance measurements were carried out using alternating current with HR 95 and PS membranes and both electrolytes. Variations of $R_m$ values with concentration for both membranes are shown in Figs. 6 and 7. Linear plots of $\ln R_m$ versus $\ln C$ were obtained with d.c. and a.c. measurements for both membranes, which agrees with the results shown in the literature [5,9]. For the porous PS membrane similar values were obtained with both types of current.

Differences between the resistances measured for HR 95 and PS membranes at the same concentrations are considered to be the resistance of the skin layer of the composite membrane $R_s$. Variations of $R_s$ with concentration for Na$_2$SO$_4$ and MgSO$_4$ solutions are drawn in Fig. 8.

Impedance spectroscopy measurements also permit us to determine the electrical resistance of a membrane for a wide range of frequencies [10]. Figure 9(a) shows the impedance plot (imaginary impedance $[-Z'']$) versus resistance [$Z'$]) obtained with the HR 95 membrane separating a 0.01 N solution of both electrolytes. Two different arcs can be seen: the large arc (marked m), which appears at the lowest frequencies (that means high relaxation time), corresponds to the membrane, and the small one (marked s) represents the electrolyte and cell geometry contributions to the impedance of the whole system. Similar curves were obtained with the PS membrane as can be seen in Fig. 9(b).

The experimental values were fitted to a circuit which consists of a series association of two parallel elements $RQ'$, one for the membrane ($R_mQ''_m$) and the other for the electrolyte contribution ($R_eQ''_e$), where $R_e$ represents the constant resistance and $Q''_e(\omega) = Q(\omega)^n$ is a fre-
quency dependent admittance. The Equivalent Circuit Program reported in Ref. [11] was used for impedance data analysis. From the electrical resistance values determined by the impedance spectroscopy method for both HR 95 and PS membranes, the resistance of the skin layer $R_s[\text{imp}]$ was also estimated for Na$_2$SO$_4$ and MgSO$_4$ solutions, and the results are drawn in Fig. 8. As can be seen from this figure, the $R_s$ values determined by the two methods do not show significant differences. A comparison of these values with those obtained for the composite membrane indicated that about 90% of the total HR 95 membrane resistance corresponds to the skin layer, which agrees with the results found with asymmetric membranes [12]. On the other hand, it is worth noting that, for the different methods used to measure the electrical resistance for the composite membrane (d.c., a.c. and impedance), higher resistance values for MgSO$_4$ than for Na$_2$SO$_4$ solutions were obtained, which also agrees with the lower $\omega_s$ value for MgSO$_4$ indicated in Table 1.

In conclusion, we can state that the experiments performed with DDSS membranes under pressure and electrical potential gradients have permitted us to determine the values of different characteristic parameters such as solute permeability and electrical resistance, of both the skin and the porous sublayer of a composite membrane when sulphate solutions are considered, which could contribute to a better understanding of the transport processes across composite membranes.

**List of symbols**

- $C$, concentration of solute
- $d_x$, element thickness
- $J_s$, solute flux
- $J_v$, volume flux
- $P$, pressure
- $P_I$, specific hydraulic permeability
- $P_l$, local solute permeability
- $R_s$, solute retention
- $R_m$, membrane electrical resistance
- $R_s$, skin layer electrical resistance
- $\pi$, osmotic pressure
- $\sigma$, reflection coefficient
- $\omega$, solute permeability

**Subscripts**
- $j$, solute $j$
- $m$, membrane
- $p$, porous layer
- $s$, skin layer

**Superscripts**
- $i$, intermediate between the skin and the porous layer
- $'$, solution facing the skin layer
- $''$, solution facing the porous layer

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