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Effect of Pressure on Some Parameters Measured with Composite and Porous Membranes

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ABSTRACT

Different transport parameters (maximum retention, hydraulic and osmotic permeabilities) for a composite membrane with Na_2SO_4 and $MgSO_4$ solutions, for concentrations ranging between 10^{-3} N and 5×10^{-2}N, were determined from reverse osmosis measurements. The influence of pressure on some characteristic parameters of the porous support, such as cation transport numbers and electrical resistance, were also studied. Differences in the values of these parameters are attributed to some changes in the structure of the porous layer due to pressure.

INTRODUCTION

Composite or asymmetric membranes used in many separation processes (ultrafiltration or reverse osmosis) are usually considered as bilayer membranes. They mainly consist of a thin and dense layer (skin layer) which determines the transport properties of the membrane as a whole, and a thick porous support to give mechanical stability to the membrane. Because of this, some transport parameters for composite membranes have been related to those obtained for each layer separately (1–3). However, the high pressure used in reverse osmosis experiments can cause some kind of compaction of the porous support, and this could affect the value of the transport coefficients in this sublayer with respect to those obtained for a similar porous membrane without the pressure effect.

In this work the transport of two electrolyte solutions (Na_2SO_4 and $MgSO_4$) through both composite and porous membranes is studied. Variation of the hydraulic and osmotic permeabilities with the concentration for the composite membrane with these electrolytes was obtained. The electrical resistance and transport numbers of two homogeneous membranes similar to the porous support of the composite membrane, one of which was previously pressurized, were also determined. Differences in values for both porous membranes show the effect of pressure on the support layer.

THEORY

When different pressure and concentration values exists on both sides of a membrane, volume (J_v) and solute (J_s) fluxes across the membrane are induced. If the fluxes are not too large, Kedem and Katchalsky obtained the following expressions (4):

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \tag{1}$$

$$J_s = (L_D - L_p\sigma^2)\langle C_s\rangle\Delta\pi + (1 - \sigma)\langle C_s\rangle J_v \tag{2}$$

where $\Delta P = P' - P''$ and $\Delta\pi = \pi' - \pi''$ are the hydrostatic and osmotic pressure differences across the membrane, respectively, L_p and L_D are the hydraulic and osmotic permeabilities, respectively, σ is the reflection coefficient, and $\langle C_s\rangle$ is the logarithmic average of the solute concentrations on both sides of the membrane.

Assuming some simplifications, Pusch (2) derived the following relationships between the salt retention (r) and the volume flux:

$$1/r = (1/r_{max}) + [(L_D/L_p) - r_{max}^2](L_p\pi'/r_{max})(1/J_v) \tag{3}$$

the salt retention being defined as $r = 1 - (C''/C')$, where C' and C'' are the feed and product concentrations, respectively, and r_{max} is the retention at infinite volume flux.

From a plot of $1/r$ versus $1/J_v$, the maximum retention r_{max} can be calculated by the intercept with the ordinate. Then, supposing that $r_{max} = \sigma$, the hydraulic permeability, L_p, can be determined by Eq. (1), and finally L_D is obtained from the slope of the straight line given by Eq. (3). In this way, some characteristic parameters of composite membranes can be easily obtained from reverse osmosis measurements.

On the other hand, when there are not pressure and temperature gradients across a membrane separating the same electrolyte at different concentrations (C_1 and C_2), an electrical potential difference, $\Delta\phi$, or "membrane potential," exists. On the basis of the Teorell–Meyer–Sievers theory (5, 6), the membrane potential (if dilute solutions are considered and activities are substituted for by concentrations) can be expressed as

$$\Delta\phi = (RT/F)\,[(t_+/z_+) - (t_-/z_-)]\,\ln(C_1/C_2) \tag{4}$$

where t_+ and t_- are the cation and anion transport numbers in the membrane (apparent transport numbers since water transport is not considered), R and F are the gas and Faraday constants, respectively, and T is the temperature of the system. Taking into account that $t_+ + t_- = 1$, Eq. (4) is also written as

$$\text{1:2 electrolyte:} \quad \Delta\phi = (RT/2F)(1 - 3t_+)\ln(C_1/C_2) \tag{5}$$

$$\text{2:2 electrolyte:} \quad \Delta\phi = (RT/2F)(1 - 2t_+)\ln(C_1/C_2) \tag{6}$$

Equations (5) and (6) represent a linear relationship between $\Delta\phi$ and $\ln(C_1/C_2)$, and by fitting the experimental point to these expressions, the apparent cation transport number in the membrane can be determined.

EXPERIMENTAL

Material

Two different kinds of membranes provided by DDSS (Dow Denmark Separation Systems) were used: a composite (polyamide/polysulfone) HR 95 and a polysulfone PS, which was the support of the composite membrane. A piece of the polysulfone membrane was pressurized at 30 atm for 5 hours; this membrane will be called PS*.

Measurements were carried out for different concentrations of Na_2SO_4 and $MgSO_4$ aqueous solutions at 25°C.

Experimental Setup

Reverse Osmosis

The composite HR 95 membrane used for reverse osmosis measurements was pressurized in the normal position (skin layer facing the high pressure side) at 50 atm for 3 hours before use to ensure stability during the experiments. The experimental system is similar to the test-cell I (without sectioning) described by Jonsson in Reference 7. The retention curves (retention versus permeate flux) were obtained with both electrolytes at different constant concentrations of the feed solution [$0.005 < C'$ (N) < 0.4] for pressures ranging between 8 and 50 atm. Concentration values for both feed (C') and permeate (C'') were determined by conductivity measurements using a Radiometer CDM3 conductivity meter.

Electrical Resistance

The electrical resistance, R_m, of both polysulfone membranes, PS and PS*, was measured with alternating current by means of a Wayne Kerr B905 Bridge and Ag/AgCl electrodes. Four different frequencies were used (f = 100, 400, 1000, and 10,000 Hz). The cell was similar to that indicated in Reference 8, and it was placed in an air-thermostat to keep the temperature constant. All measurements were made with the membranes in the membrane holder and without them, and the difference between these values was taken as the membrane impedance as indicated in Reference 9. For both electrolytes R_m values at different concentrations were obtained [$0.001 < C$ (N) < 0.05], but in each case the concentration at both sides of the membrane had the same value ($C_1 = C_2 = C$).

Membrane Potential

The membrane potential experimental device was reported in Reference 10. Membrane potential measurements were carried out with PS and PS* membranes while keeping the concentration of the solution constant on one side of the membrane while the concentration of the solution on the other side was gradually increased. Values for the constant concentrations were C_2 = 0.001, 0.005, 0.01, and 0.02 N. The membrane potential, $\Delta\phi$, was measured with calomel electrodes joined to the solutions on both sides of the membrane via saline bridges. $\Delta\phi$ values were corrected to compensate for electrode asymmetry but not for the liquid junction potential at the tips of the saline bridges.

RESULTS AND DISCUSSION

From reverse osmosis measurements with the composite membrane, salt retention as a function of the volume flux was obtained. The experimental values at different Na_2SO_4 and $MgSO_4$ feed concentrations are drawn in Fig. 1. Salt retention values were corrected for concentration-polarization at the membrane/electrolyte interface, as described in Reference 7. For both electrolytes, activity retention was considered ($r_a = 1 - [C'\gamma''/C''\gamma']$), and a decrease of r_a with increasing concentration was found. By fitting these experimental points while taking into account the Kedem–Katchalsky expression with appropriate boundary conditions (11), the membrane retention coefficient, σ, for each electrolyte was determined (12). The σ values obtained for each concentration and electrolyte are listed in Table 1.

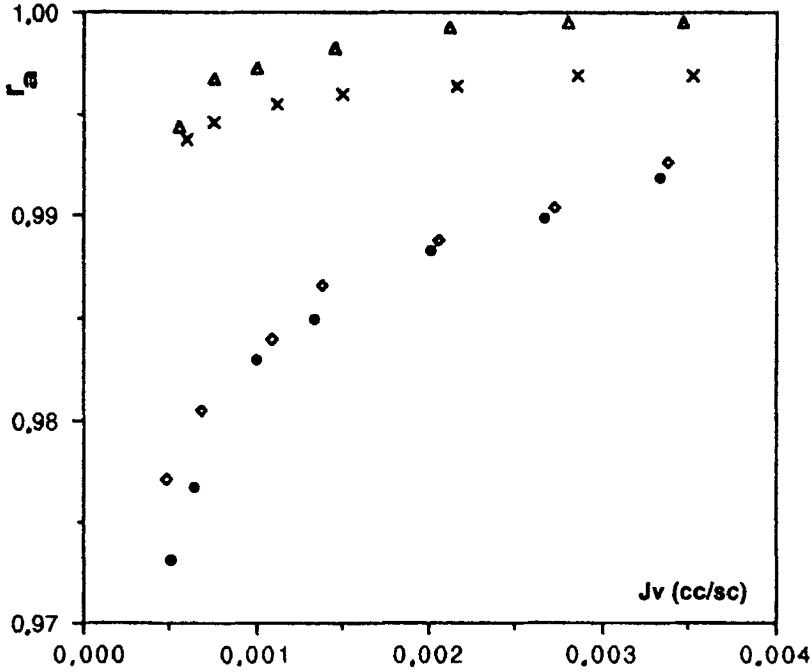

FIG. 1 Salt retention versus permeate flux for the HR 95 composite membrane at different concentrations. Na_2SO_4: (×) 0.005 N and (●) 0.05 N. $MgSO_4$: (△) 0.005 N and (◇) 0.05 N.

TABLE 1

Variation of the Reflection Coefficient, σ, and the Maximum Retention, r_{max}, with Salt Concentration for Na_2SO_4 and $MgSO_4$ Solutions

Salt concentration (N)	Na_2SO_4		$MgSO_4$	
	σ	r_{max}	σ	r_{max}
0.005	0.9977	0.9986	0.9996	0.9998
0.01	0.9988	0.9976	0.9995	0.9989
0.05	0.9974	0.9944	0.9980	0.9928
0.10	0.9983	0.9951	0.9977	0.9887
0.20	0.9973	0.9934	0.9977	0.9850
0.40	0.9970	0.9903	0.9980	0.9845
	$\langle\sigma\rangle$	$\langle r_{max}\rangle$	$\langle\sigma\rangle$	$\langle r_{max}\rangle$
	0.9978 ± 0.0006	0.995 ± 0.003	0.9984 ± 0.0008	0.992 ± 0.006

Figures 2 and 3 show $1/r_a$ versus $1/J_v$ at different constant values of the feed concentration for Na_2SO_4 and $MgSO_4$ solutions respectively. By fitting these experimental points with the minimum squares method, r_{max} can be determined and, according to Eqs. (1) and (2), L_p and L_D values are also obtained. Variation of r_{max} with concentration is also indicated in Table 1. The average values of both the reflection coefficient, $\langle\sigma\rangle$, and the maximum retention, $\langle r_{max}\rangle$, are also given in Table 1. The assumption that $r_{max} = \sigma$, which is necessary for L_p determination using Eq. (1), as indicated above, is established in both cases, as can be seen by comparison of the results presented in Table 1.

Variation of the parameters L_p and L_D with feed concentration for the composite membrane are shown in Figs. 4 and 5 for both electrolytes. Similar kinds of dependences are indicated in the literature for both parameters with asymmetric cellulose acetate membranes and NaCl solutions (13). From these figures some differences in both L_p and L_D values at low

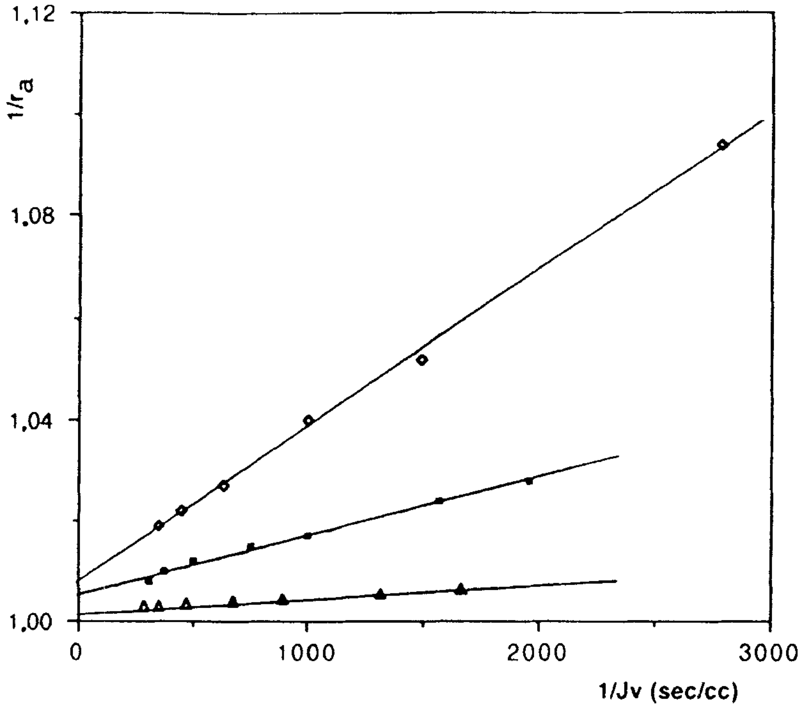

FIG. 2 Variation of $1/r_a$ with $1/J_v$ for the HR 95 membrane at different Na_2SO_4 concentrations: 0.005 N (◇), 0.05 N (■), 0.2 N (△).

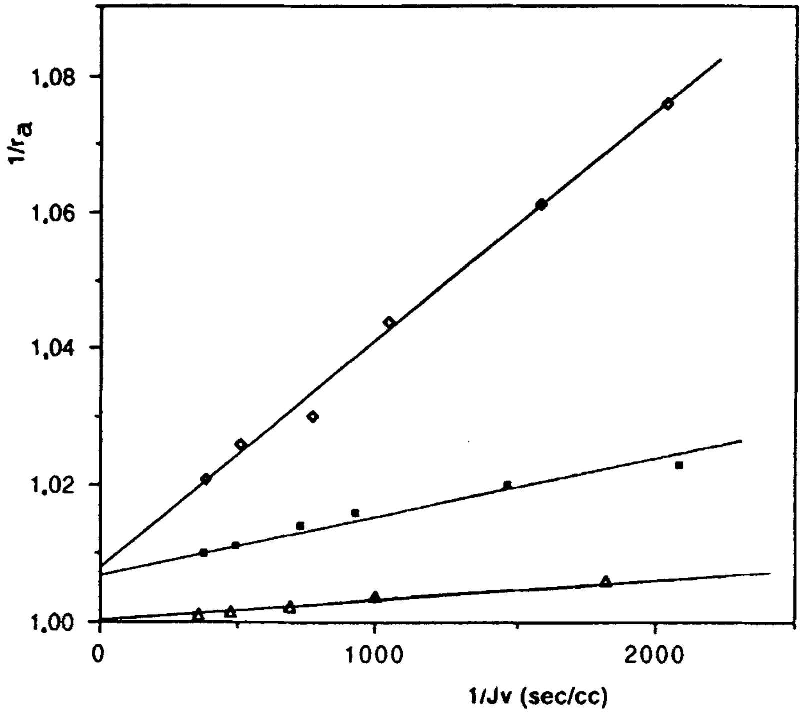

FIG. 3 Variation of $1/r_a$ with $1/J_v$ for the HR 95 membrane at different $MgSO_4$ concentrations: 0.005 N (◇), 0.05 N (■), 0.2 N (△).

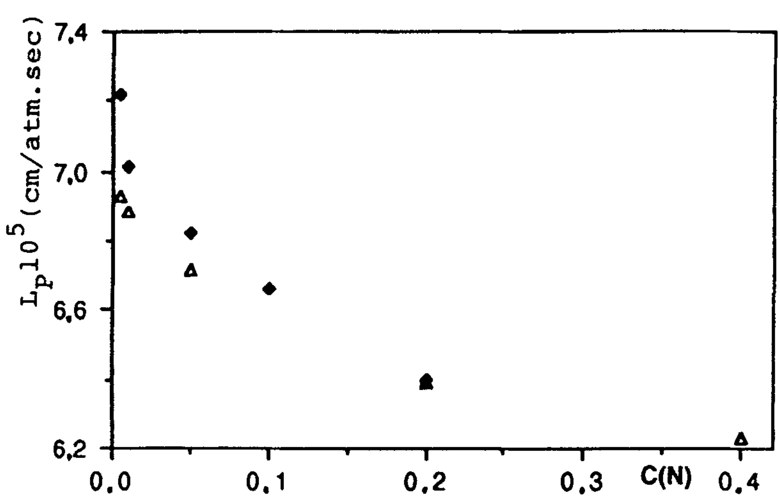

FIG. 4 Hydraulic permeability coefficient, L_p, versus feed concentration for the HR 95 membrane: (△) Na_2SO_4, (◆) $MgSO_4$.

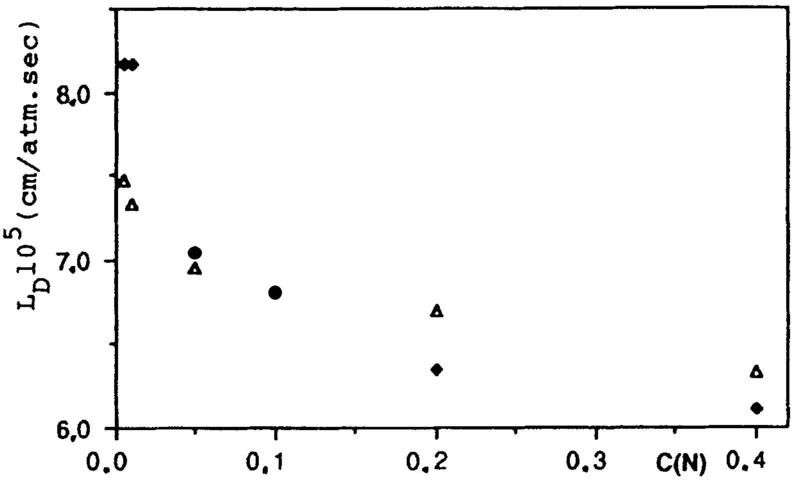

FIG. 5 Osmotic permeability coefficient, L_D, versus feed concentration for the HR 95 membrane: (△) Na_2SO_4, (◆) $MgSO_4$.

concentrations depending on the electrolyte can be observed, but at high concentrations the values are more similar.

Cation transport numbers for both porous membranes and electrolytes were calculated from membrane potential measurements using Eqs. (5) and (6). Figures 6 and 7 show the dependence of t_+ values with the average concentration ($C_{av} = [C_1 + C_2]/2$) for Na_2SO_4 and $MgSO_4$ solutions at different values of the constant concentration, C_2. A decrease of t_+ values when C_{av} increases is observed in all cases, but it is more significant at low concentrations; at high concentrations almost constant values of t_+ are reached. These values are slightly higher than those corresponding to free solution, which indicates some influence of the membrane in the diffusion process. Some differences in the values of the cation transport numbers for PS and PS* membranes were found for both electrolytes.

Variation of the electrical resistance with concentration ($\ln R_m$ vs $\ln C$) at two different frequencies ($f = 100$ and 10,000 Hz) are drawn in Figs. 8 and 9 for PS and PS* membranes with Na_2SO_4 and $MgSO_4$ solutions, respectively. For both membranes the resistance values decrease when the concentration increases, but at low concentrations the decrease is about 25–30% of the average R_m value while at high concentrations it is less than 10%. This fact could be related to the influence of the concentration polarization layers at the membrane/solution interfaces. From both illustrations some differences in the electrical resistance values measured

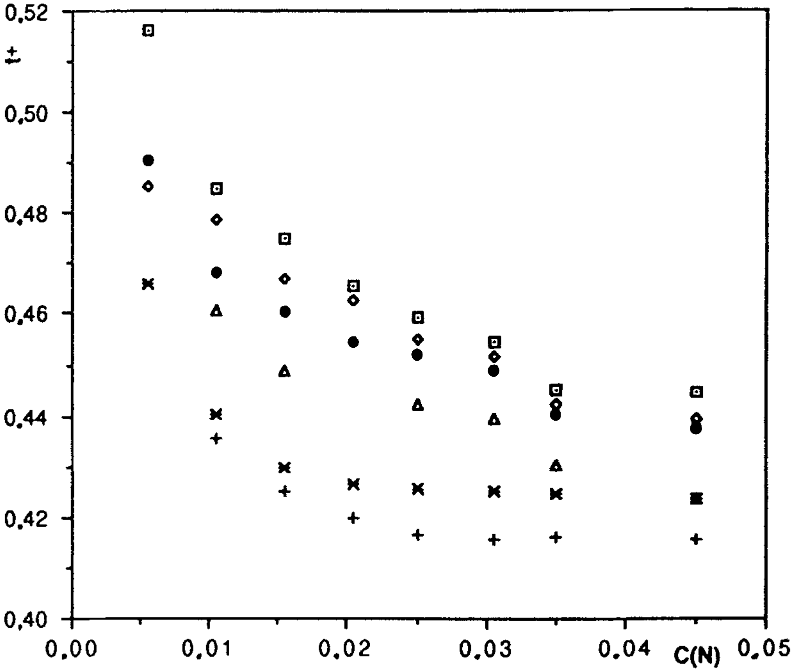

FIG. 6 Apparent cation transport number, t_+, in the PS and PS* membranes as a function of the average concentration, C_{avg}, determined at different Na_2SO_4 constant concentrations. Membrane PS: (□) 0.001 N, (●) 0.01 N, and (△) 0.02 N. Membrane PS*: (◇) 0.001 N, (*) 0.01 N, and (+) 0.02 N.

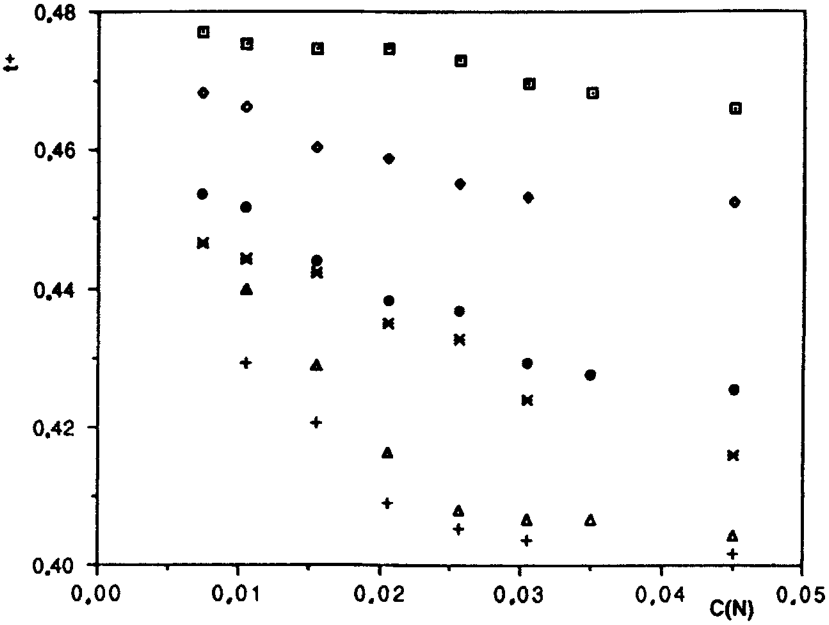

FIG. 7 Apparent cation transport number, t_+, in the PS and PS* membranes as a function of the average concentration, C_{avg}, determined at different $MgSO_4$ constant concentrations. Membrane PS: (□) 0.001 N, (●) 0.01 N, and (△) 0.02 N. Membrane PS*: (◇) 0.001 N, (*) 0.01 N, and (+) 0.02 N.

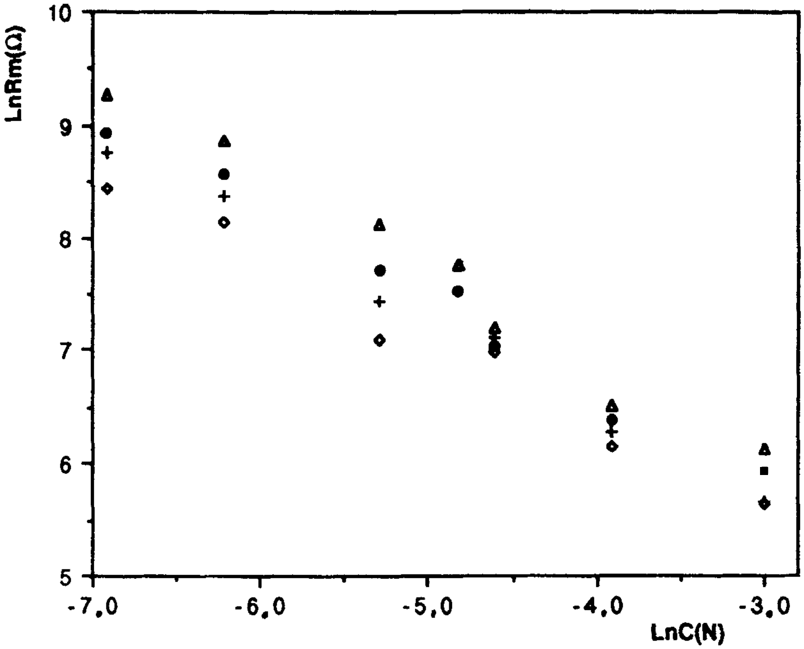

FIG. 8 Variation of the electrical resistance (ln R_m) with Na_2SO_4 concentration (ln C) for both porous membranes at two different frequencies. Membrane PS: (△) f = 100 Hz, (●) f = 10 kHz. Membrane PS*: (+) f = 100 Hz; (◇) f = 1 kHz.

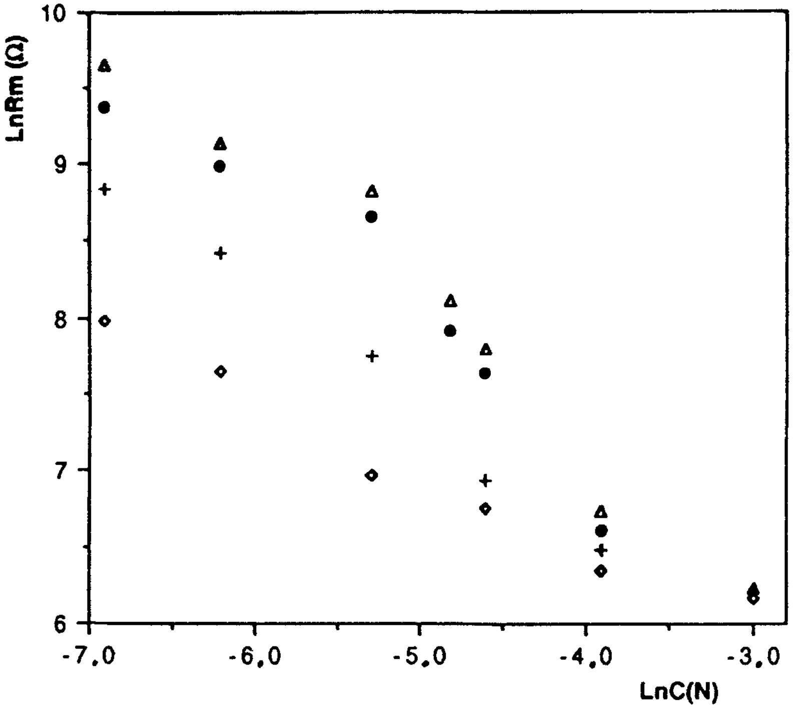

FIG. 9 Variation of the electrical resistance (ln R_m) with $MgSO_4$ concentration (ln C) for both porous membranes at two different frequencies. Membrane PS: (△) f = 100 Hz, (●) f = 10 kHz. Membrane PS*: (+) f = 100 Hz; (◇) f = 1 kHz.

with both porous membranes can be seen. The influence of the frequency in R_m values for both PS and PS* membranes is also indicated in these figures: when the frequency increases, the resistance decreases, but this influence is weak at high concentrations. This fact can be attributed to a kind of concentration polarization due to the membrane barrier effect, which should be more evident at low concentrations.

Changes in both t_+ and R_m values for PS and PS* membranes are attributed to some compaction in the structure of the porous membrane due to pressure. These results indicate that the pressure gradient used in reverse osmosis experiments may slightly change the structure of the porous support and, additionally, the value of some of the transport parameters determined in the absence of pressure.

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