Transport of NaCl, MgSO$_4$, MgCl$_2$ and Na$_2$SO$_4$ across DL type nanofiltration membrane

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Abstract

The separation of inorganic ions by membrane filtration of aqueous solutions through NF-membranes was investigated. The single and binary salt solutions of NaCl, MgCl$_2$, Na$_2$SO$_4$ and MgSO$_4$ were used in this study. These salts are the most commonly found in natural water resources. From the research literature it was stated that NaCl has a very low rejection range with NF membranes while MgCl$_2$ is moderately rejected, Na$_2$SO$_4$ and MgSO$_4$ are very highly rejected salts. Thus, these four salts provide a full range of rejection behavior for the NF system and hence constitute an ideal system. In addition, these salts have a very high solubility in water so there would not be any cake layer formed due to precipitation of salts at the surface of the membrane where a significantly higher concentration of salt can be developed due to concentration polarization.

Keywords

Nanofiltration; Salt separation

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1 Introduction

The aim of our research is to investigate the effect of an accompanying anion on the NF separation of cations by the aid of a DL membrane which is commercially available. For this reason we investigated simple bivalent and monovalent ions (Na$^+$, Mg^{2+}, Cl$^-$, SO$_4^{2-}$).

Nanofiltration (NF) can be used to concentrate solutions containing multivalent salts or to fractionate salts due to the different charge densities and hydrated sizes of the ions [1–3].

Charge effects are important in salt separation using NF, for which both sieving and solution-diffusion are the major separation mechanisms [4].

The most important feature of the experimental separation data is the effect of the anion valence and the feed concentration on the salt rejections. For a given set of operating conditions, the salt rejections (R) follows the order: $R_{MgCl_2} < R_{MgSO_4} < R_{Na_2SO_4}$. These two facts, typical of electrically charged membranes, are qualitatively in agreement with the ion exclusion principle [5–7]. The idea of using membrane separation as a method to concentrate Na$_2$SO$_4$ solutions from brine streams was first conceived in 1992, and between 1993-1995 the performance of a variety of commercially available NF membranes was tested using a specially designed test apparatus in Kvaerner Chemetics' laboratory. NF membranes have previously been shown to effectively separate multivalent anions, (e.g. SO$_4^{2-}$) from monovalent ones, (e.g. Cl$^-$) in dilute solutions [8]. Already in 1990, Rautenbach and Gröschl reported a significant decrease in NaCl retention when Na$_2$SO$_4$ was added to the feed solution [9]. Similar effects have also been reported when acidic salt solutions were filtered: nitric acid and sodium nitrate permeation was enhanced by the addition of magnesium nitrate and in a separate study, sulphuric acid permeation was enhanced by the addition of copper sulphate [10, 11].

2 Experimental

The aim of our investigation was the study of the NF separation of Na$^+$ and Mg^{2+} ions effected by the various of accompanying anions. All the salt solutions were prepared from Ul-

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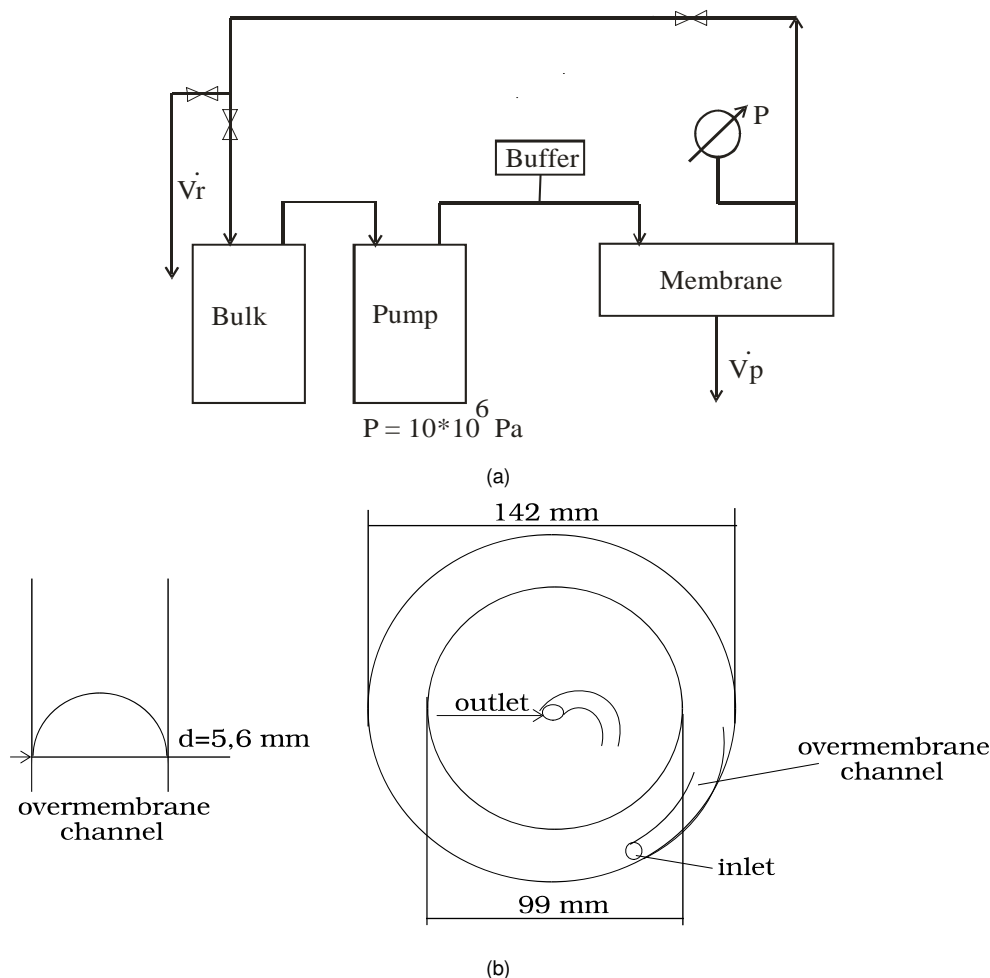**Fig. 1.** (a) The experimental set. (b) Cell dimensions

tra Pure Water (UPW) with an ionic conductivity of 0.05 μS/m at 24°C and high purity salts NaCl, MgCl$_2$.6H$_2$O, Na$_2$SO$_4$ and MgSO$_4$.7H$_2$O purchased by Aldrich. The purified water utilized to prepare the feed solutions minimizes the biological growth before and during the experiments and also prevents the intrusion of extraneous substances in the feed solutions. In the experiments we used neutral Ph solutions. Our experimental arrangement is shown in Fig. 1(a).

A commercially available flat NF membrane of a DL type was used (15% sodium chloride retention given for 4 MPa, membrane constitution not published). The characteristics of these membranes are shown in Table 1.

Dimensions of the membrane holder (supplied by Kutesz Co, Hungary) are shown in Fig. 1(b). The membrane holder, the pump and the valves were constructed of stainless steel, and connected with polyamide tubing.

Tab. 1. Characteristics of the NF membrane used

Membrane	company	MWCO (Da)	Material	Recommended pH range
DL	DESAL	490	polyamid	2-11

In our experiments we circulated a bulk solution with the concentrate recirculation monitoring the nearly constant composi-

tion of the permeate as a function of time, until a steady state was achieved. In each separation experiment we used a constant feed flow rate 7.8 10^{-3} m^3/h and the concentrate was recirculated to the feed tank.

Fig. 2 shows the concentrate and permeate concentrations as a function of time. According to the figure the permeate concentrations are changing slightly and reaching a steady value, while the concentrate concentration is increasing during all experiments.

3 Analytical methods

The sodium and magnesium content was measured by ion chromatography. (type: Metrohm 861 Advanced compact IC, Metrohm 837 IC combi degasser, Metrohm 771 IC compact interface, Metrosep C3 250 cation exchange column, eluent: 5.0 mM HNO$_3$, conductivity detector). The chloride and sulphate concentration was measured by ion chromatography using a Metrosep A Supp 4. 250/4.0 anion exchange column and 1.8 mM Na$_2$CO$_3$ and 1.7 mM NaHCO$_3$ solutions after the preceding calibration.
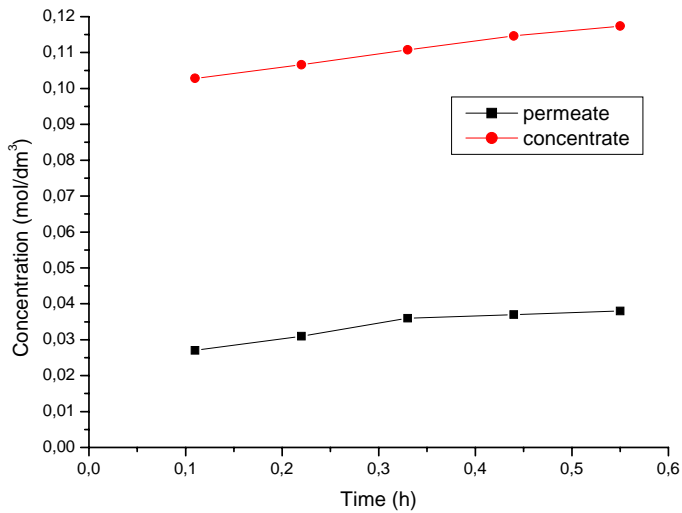
Fig. 2. Evolution the concentrate and permeate concentration as a function of time

4 Calculations

Transmission (Tr) of components through the NF membrane was calculated according to Eq. (1):

$$Tr(\%) = \frac{C_p}{C_r} \cdot 100 \qquad (1)$$

where C_p[mol/dm^3] is the concentration of a component in the permeate and C_r[mol/dm^3] the concentration of the same component in the retentate.

5 Results

A predetermined quantity of salt was mixed in a known volume of deionized water to prepare the feed solution of desired concentration. These salts have a very high solubility in water at room temperature (22~26 ^{0}C) so there would not be any cake layer formed due to precipitation of salts at the surface of membrane where significantly higher concentration of salt can be developed due to concentration polarization.

5.1 Investigation of NaCl solution

First we conducted the nanofiltration of UPW water containing 0.1 mol/dm^{3}NaCl through the DL nanofiltrating membrane. We measured the sodium and chloride ion concentrations and calculated the transmission values by Eq. (1) (Table 2) we created a graph using the measured data, which showed the single ion transmission in relation to the volume of the permeate (Fig. 3).

In case of NaCl separation the curves of the single ion transmission of the sodium and chloride ions overlap, indicating that the sodium and chloride ions are passing the membrane together. It is clear from the experiment, that the transmission of the Na$^+$as well as the Cl$^-$ ions through the nanofiltration membrane are high.

5.2 Investigation of MgCl$_2$ solution

The MgCl$_2$solution can be considered as a type 2-1 system: it consists of a bivalent cation and two monovalent anions. Ac-

Tab. 2. NaCl transmission in the DL membrane (t= 25 ^{o}C, p=10 bar)

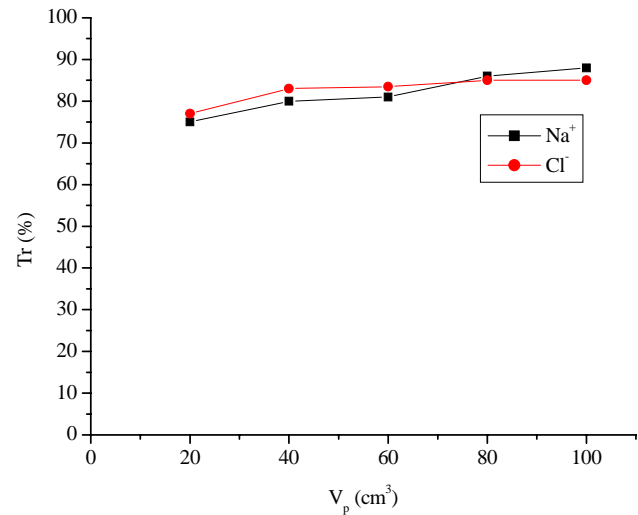| The volume of permate Vp(cm^3)	Tr$_{(Na^+)}$ (%)	Tr$_{(Cl^-)}$ (%)
20	75	77
40	80	83
60	81	83.5
80	86	85
100	88	85

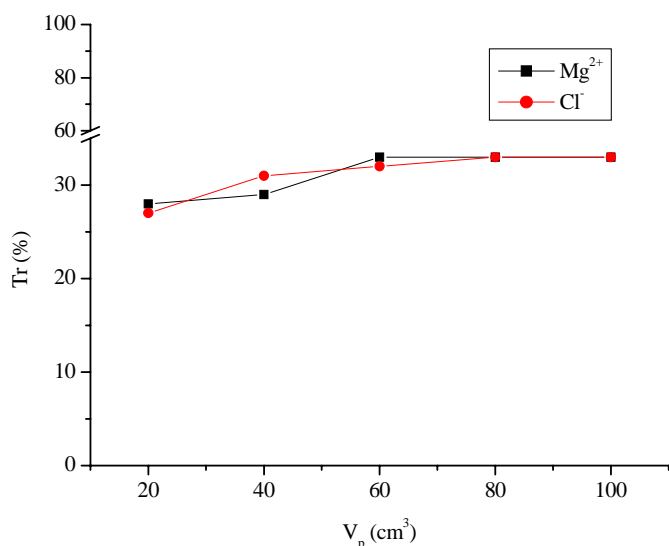**Fig. 3.** NaCl transmission as a function of the volume of permate

cording to the data in the literature, in the case of multivalent ions, the ion transmission through the NF membranes is significantly lower than that of the monovalent ions. It may sound surprising that although magnesium is bivalent and is a relatively large cation, its ion transmission is highly siginficant through NF membranes. The explanation of this phenomenon is that a tension difference occurs on the membrane in the beginning of the diffusion process. As the diffusion coefficient of the chloride ions measured at the water solution is much larger than that of the magnesium ions (Table 3), in a given period of time of the ions on the larger concentration side of the membrane, the chloride ions get further within the membrane than the magnesium ions. Thus, an electric field develops and the initially smaller concentration side will be more negative than the other side. This field will slow down the diffusion of the chloride ions and accelerate that of the magnesium ions. This field is called a diffusion field. The diffusion field facilitates the diffusion of the chloride ions and magnesium ions to diffuse with nearly the same rate (Table 4 and Fig. 4).

Tab. 3. Diffusion constant of some ions measured in water solution at 25 ˚C [12, 13]

Ion	D$_0$ (x 10^{-10} m^2/s)
Na$^+$	13,3
1/2Mg^{2+}	7,05
Cl$^-$	20,3
1/2SO$_4^{2-}$	10,7

Tab. 4. MgCl$_2$ transmission in the DL membrane (t= 25 ^{o}C, p=10 bar)

The volume of permate Vp(cm^3)	Tr$_{(Mg^{2+})}$ (%)	Tr$_{(Cl^-)}$ (%)
20	28	27
40	29	31
60	33	32
80	33	33
100	33	33

Tab. 5. Na$_2$SO$_4$ transmission in the DL membtane (t= 25 ^{o}C, 10 bar)

The volume of permate Vp(cm^3)	Tr$_{(Na^+)}$ (%)	Tr$_{(SO_4^{2-})}$ (%)
20	5.0	4.5
40	6.0	5.0
60	6.7	5.3
80	7.0	5.5
100	7.0	5.8

Fig. 4. MgCl$_2$ transmission as a function of the volume of permate

Fig. 5. Na$_2$SO$_4$ transmission as a function of the volume of permate

In the case of MgCl$_2$ separation, the curves of the single ion transmission of the magnesium and chloride ions overlap, indicating that the cation goes through the membrane at the same time as the anions. It is clear from the experiment that the transmission of the Mg^{2+} comma goes here as well as the Cl$^-$ ions through the nanofiltration membrane are not too high.
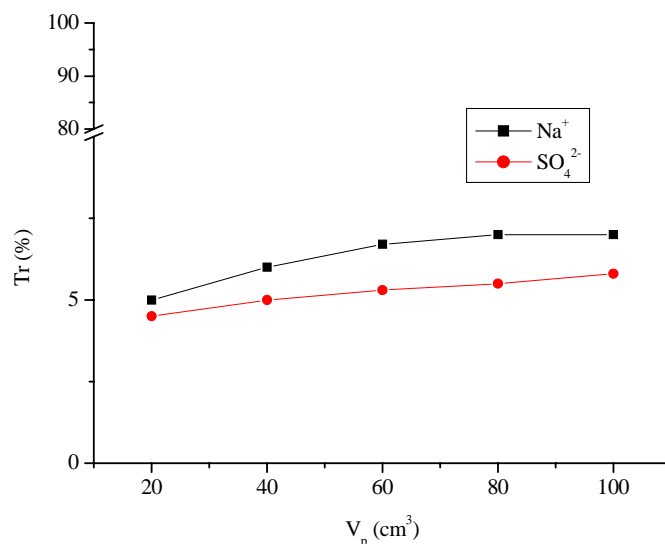
5.3 Investigation of Na$_2$SO$_4$ solution

The Na$_2$SO$_4$solution is a type 1-2 system. It is seen from the transmission curves (Fig. 5) that the transmission of the ions is determined by the bivalent and large sized sulphate ion. The transmission of the sodium ion through the DL type membranes is under 7%. As the diffusion constant measured in water solution of the sulphate ions is smaller than that of the sodium ions (Table 3), in a given period of time of the ions on the membrane concentrate, sodium ions get further within the membrane than the sulphate ions. Thus an electric field will develop and initially one side of the permeate will be more positive than the other. This field will slow down the diffusion of the sodium ions and accelerate that of the sulphate ions. From this it is evident that the sulphate ions slow down the transmission of the sodium ions through the membrane (Table 5).

It is evident from the experiments that the transmission of the Na$^+$ and the SO$_4^{2-}$ ions through the nanofiltration membrane is low.

5.4 Investigation of MgSO$_4$ solution

MgSO$_4$ is a 2-2 system. It is seen from the measured ion transmission curves (Fig. 6) that the ion transmission is very small through the DL type membrane for both the magnesium ions and the sulphate ions. The sulphate ion has a slowing effect on the transmission of the magnesium ion. We made a graph using the measured data, on which the specific ion transmissions can be seen together with the curve of the permeate volume (Table 6).

Tab. 6. MgSO$_4$ transmission in the DL membrane (t= 25 ^{o}C, p=10 bar)

The volume of permate Vp(cm^3)	Tr$_{(Mg}^{2+)}$ (%)	Tr$_{(SO_4^{2-})}$ (%)
20	2.3	3.0
40	2.3	2.6
60	2.4	2.5
80	3.0	2.5
100	3.0	2.6

In case of MgSO$_4$ separation the curves of the specific ion transmissions are overlapping, showing that the cations get through the membrane together with the anions. It is evident from the experiments that the transmission of the Mg^{2+} and the SO$_4^{2-}$ ions through the nanofiltration membrane is low.

Fig. 6. MgSO$_4$ transmission as a function of the volume of permate
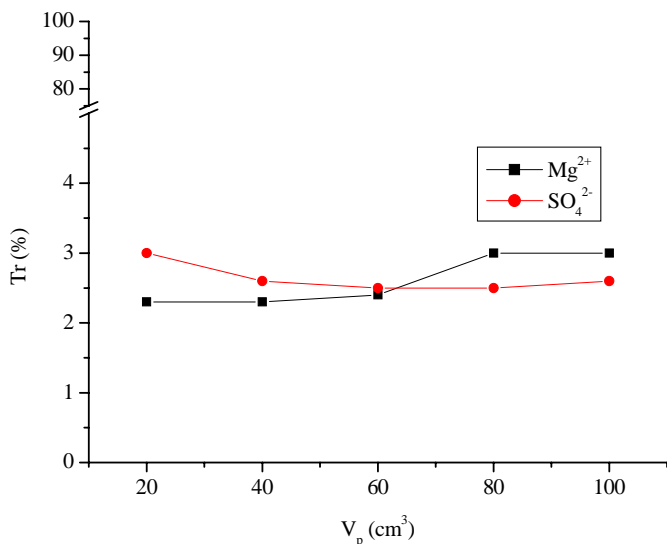

Fig. 7. NaCl and MgSO$_4$ transmission as a function of the volume of permate

5.5 Investigation of the mixture of NaCl and MgSO$_4$ solutions

In this part of the experiment we made a mixture of 0.1 mol/dm^3 NaCl solution (1-1 system) and of 0.1 mol/dm^3 MgSO$_4$ solution (2-2 system) and conducted the experiment under pressure of 10 bar. The measurement data and results are shown in Table 7 and Fig. 7.

Tab. 7. NaCl and MgSO$_4$ transmission in the DL membrane (t= 25 ^{o}C, p=10 bar)

The volume of permate Vp(cm^3)	Tr$_{(Na+)}$ (%)	Tr$_{(Mg^{2+})}$ (%)	Tr$_{(Cl^-)}$ (%)	Tr$_{(SO_4^{2-})}$ (%)
20	68	12	81	3.0
40	72	13	87	2.6
60	71	15	88	2.3
80	73	8	89	2.4
100	73	7	90	2.5

The transmission of the sulphate and magnesium double charged ions is smaller than that of the sodium and chloride ion. The transmission of magnesium in this multicomponent a solution is higher than in a single MgSO$_4$ solution (Table 6). The explanation to this phenomenon is that the original ions from the dissolved salts (MgSO$_4$, NaCl) are slightly exchanged, i.e., some magnesium passed the membrane with two chloride anions.

5.6 Investigation of the mixture of MgCl$_2$ and Na$_2$SO$_4$ solutions

For this experiment we made a 0.1 mol/dm^3 MgCl$_2$(2-1) system and a 0.1 mol/dm^3 Na$_2$SO$_4$(1-2) system solution. When all four ions (Na$^+$, Mg^{2+}, Cl$^-$, SO$_4^{2-}$) are in the solution, the differences between the monovalent and bivalent ions become clearly visible. The measurement data and results are shown in Table 8 and Fig. 8.
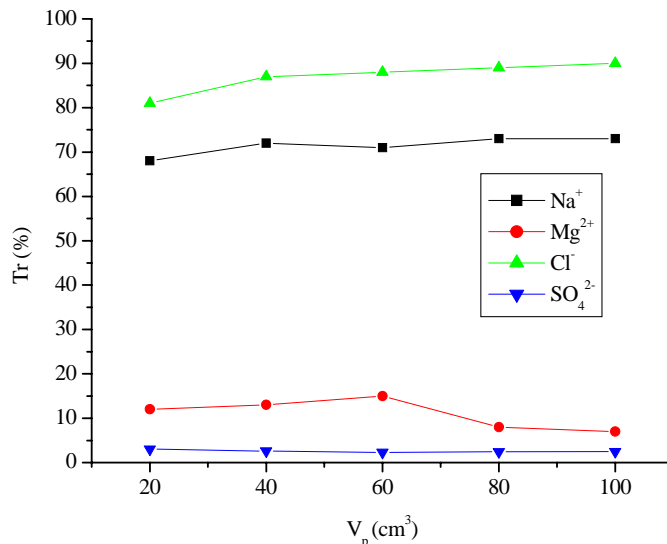
Tab. 8. MgCl$_2$ and Na$_2$SO$_4$ transmission in the DL membrane (t= 25 ^{o}C, p=10 bar)

The volume of permate Vp(cm^3)	Tr$_{(Na+)}$ (%)	Tr$_{(Mg^{2+})}$ (%)	Tr$_{(Cl^-)}$ (%)	Tr$_{(SO4^{2-})}$ (%)
20	68	10	83	2
40	72	10	91	2
60	75	9	91	2
80	75	9	90	2
100	75	9	89	2

This experiment had interesting results. The transmission of chloride and sodium in the multicomponent solution is higher than for pure MgCl$_2$ solution and Na$_2$SO$_4$ solution (Tables 4 and 5). The explanation to this phenomenon is that the original ions from dissolved salts are heavily exchanged, i.e., most of the sodium crosses the membrane with a chloride anion.

6 Conclusions

In the case of bivalent ions, irrespective of their charge, the ion transmission is smaller than in the case of the monovalent ions. In the course of the experiments we found that during the creation of the multicomponent solution (MgCl$_2$, Na$_2$SO$_4$, NaCl and MgSO$_4$) a ligand exchange happened between MgCl$_2$ and Na$_2$SO$_4$. The two anions changed places (ligandum change) and large ion pairs were created which goes through the membrane with difficulty.

These phenomena observed could cause a new possibility of increasing the separation efficiency of monovalue ions from a multicomponent system by the aid of nanofiltrating membranes. These results can be applied for example, in the treatment of regeneration solutions of sodium cycle ion exchanges using nanofiltration, and in the treatment of galvanic industry wastewater.
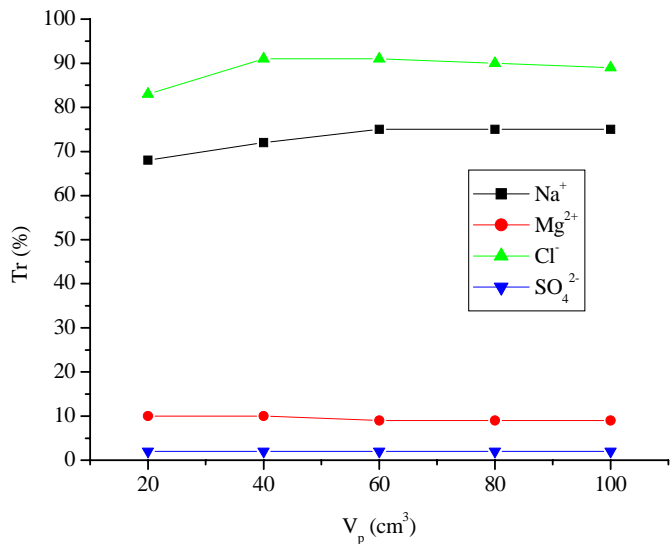
Fig. 8. MgCl$_2$ and Na$_2$SO$_4$ transmission as a function of the volume of permate

7 Nomenclature

C (mol/ dm^3):	Ion concentration in the feed
C$_p$ (mol/ dm^3):	Ion concentration in the permeate
C$_r$ (mol/ dm^3):	Ion concentration in the retentate
Tr (%):	Ionic transmission
V$_p$(m^3/h):	Flow of the permeate
V$_r$(m^3/h):	Flow of the retentate
Vp (cm^3):	Volume of the permate

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