

Transport Properties of Perfluorinated Cation-Exchange Membranes in Aqueous and Methanol Solutions of NaCl

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The properties of perfluorinated membranes (Nafion[®]) with sulfonic and carboxylic groups in aqueous and methanol solutions of NaCl at room temperature is compared. The transport properties examined are: the apparent transport number of Na⁺, conductivity, permeability of electrolyte and the solvent. It is found that the decrease of separating ability of membranes in methanol solutions is caused mainly by the increase of solvent and salt permeability. The transport numbers of Na⁺ counterions in both solvents are comparable. The highest increase of permeation rates of salt and solvent is observed for the carboxylate membrane.

Key words: membranes, transport number, conductivity, diffusion, osmosis

The perfluorinated ion-exchange membranes are widely used as separators in many processes (electrosynthesis, energy transformation in fuel cells, catalysis, *etc.* [1–4]). The growing applications of these membranes are caused by their outstanding properties (high selectivity, exceptional chemical stability in alkali and oxidizing media at wide range of temperature). Some attempts of application of perfluorinated membranes in solvents other than water are met in literature [5–7]. The swelling properties of these membranes are well recognized [8–10], but still the data on their transport behaviour are poor [11, 12]. One of the solvents in which the membrane could be potentially used seems to be methanol which appears in electrosynthesis of methanolates [5], dimethoxylation of furan [6]. To test the applicability of the perfluorinated membranes in methanol media the basic transport properties (conductivity, transport number, diffusion and osmosis) in methanol solutions of sodium

chloride at room temperature were measured and compared with those in aqueous media. For the investigation three types of Nafion[®] membranes have been chosen: sulfonate Nafion[®] 117 (here denoted as N117), carboxylate film (NCR), two layer membrane (NSCR) consisting of 4 mil sulfonate and 1 mil carboxylate layers.

EXPERIMENTAL

The membranes denoted by NCR and NSCR were hydrolyzed according to the prescription of manufacturer. All the membranes (Na⁺-form) were pretreated by boiling in water for an hour and dialysed with *ca.* 0.5 m NaCl. The same samples of membranes were used in aqueous and methanol solutions. After the measurements in aqueous solutions the membranes were washed several times in methanol for a week, then placed in *ca.* 0.1 m NaOMe solution, and again washed with methanol. In the transport experiments the carboxylic side of NSCR membrane always faced the dilute solution. All measurements were performed at 25°C. Because of low solubility of NaCl in methanol, the concentration range of methanol solutions was 0–0.2 m.

Swelling

The swelling of the membranes was determined by weighting the membranes in swollen and dry states. The membranes were dried under vacuum at room temperature and then at 110°C until the constant weight.

Apparent transport number

The apparent transport number of cations, $\bar{t}_{1,app}$, was calculated by the emf of the membrane concentration cell in the small concentration intervals covering the investigated concentration range [13]. The silver–silver chloride electrodes, prepared according to [14], were used. The curve

$$E_i(m^{(0)} \rightarrow m^{(i)}) = \sum_{k=1}^i \Delta E_k(m^{(k-1)} \rightarrow m^{(k)}) \quad (1)$$

was approximated by a cubic spline as a function of $\ln(m\gamma_{\pm})$ and then differentiated to yield $\bar{t}_{1,app}$

$$\bar{t}_{1,app} = -z_1 v_1 \frac{\partial E}{\partial \mu_s} = \frac{F}{2RT} \frac{\partial E}{\partial \ln(m\gamma_{\pm})} \quad (2)$$

Here m denotes molality, γ_{\pm} – mean activity coefficient of the electrolyte in the solution [15–18].

Conductivity

The conductivity of membranes was determined by the ac method using a thermostated cell with a constant distance between Pt electrodes. The specific conductivity of a membrane, κ_m , was calculated having measured the resistance of the cell with, R_{m+e} , and without a membrane, R_e :

$$\kappa_m = ((R_{m+e} - R_e)A_m + d_m/\kappa_e)^{-1} \quad (3)$$

In (3) A_m , d_m , κ_e denote area, thickness of the membrane, conductivity of the solution, respectively.

Permeability of electrolyte

The flow of NaCl across a membrane, J_s , was determined by measuring the time changes of conductivity of the dilute solution side ($c_s^{(0)} \approx 0.003$ mol/dm³). The measurements were performed for different concentrations of NaCl on the more concentrated side (c_s). The permeability of electrolyte, P_s , was calculated according to Meares' method [19], as the concentration derivative of J_s :

$$P_s = d_m \left(\frac{\partial J_s(c_s \rightarrow c_s^0)}{\partial c_s} \right)_{\Delta p, l=0} \quad (4)$$

Osmotic permeability

The volume osmotic flux, J_v , was determined by volumetric method. The osmotic permeability, P_{osm} , was calculated following the relation:

$$P_{osm} = d_m \left(\frac{\partial J_v}{\partial c_s} \right)_{\Delta p, l=0} \quad (5)$$

J_v in (5) is the sum of osmotic flows measured in narrow concentration intervals:

$$J_v = \sum_k J_v(c_s^{(k-1)} \rightarrow c_s^{(k)}) \quad (6)$$

RESULTS AND DISCUSSION

Swelling

The basic properties of membranes are shown in Table 1.

Table 1. Basic properties of the investigated membranes.

Membrane	N117		NSCR		NCR	
ion-exchange group	-SO ₃ ⁻		-SO ₃ ⁻ /-COO ⁻		-COO ⁻	
ion-exchange capacity ($\frac{\text{mole fixed charge}}{\text{kg dry membrane}}$)	1.02		0.96		0.80	
Solvent	MeOH	H ₂ O	MeOH	H ₂ O	MeOH	H ₂ O
Swelling ($\frac{\text{mol solvent}}{\text{mol fixed charge}}$)	20.9	15.4	18.3	15.2	16.9	9.3
Thickness (mm)	0.24	0.2	0.17	0.15	0.075	0.05

The general tendency, observed also by other authors [9, 10], is that perfluorinated ion-exchange membranes swell better in methanol than in water. The difference results from the macroscopic structure of these membranes, where three regions of different polarity can be distinguished (Fig. 1) [20]. The fixed charges, at the end of pendant chains, form the clusters, region of the highest polarity, which contains the main part of the solvent. The region of the ether bridges is less polar and is stronger penetrated by methanol (less polar solvent, dielectric constant $\epsilon_r = 32.7$) than by water ($\epsilon_r = 78.3$). The nonpolar fluorocarbon matrix is not penetrable by water, but can be to some extent penetrated by methanol. The swelling of membranes depend strongly on the conditioning of membranes before experiments. Nandan *et al.* [9], who did not expand the membranes by boiling in a solvent, observed *ca.* 50 % smaller sorption of solvents into the Nafion 117 membrane (Na⁺-form: $N_s = 13.5$ (MeOH), 7.6 (H₂O)).

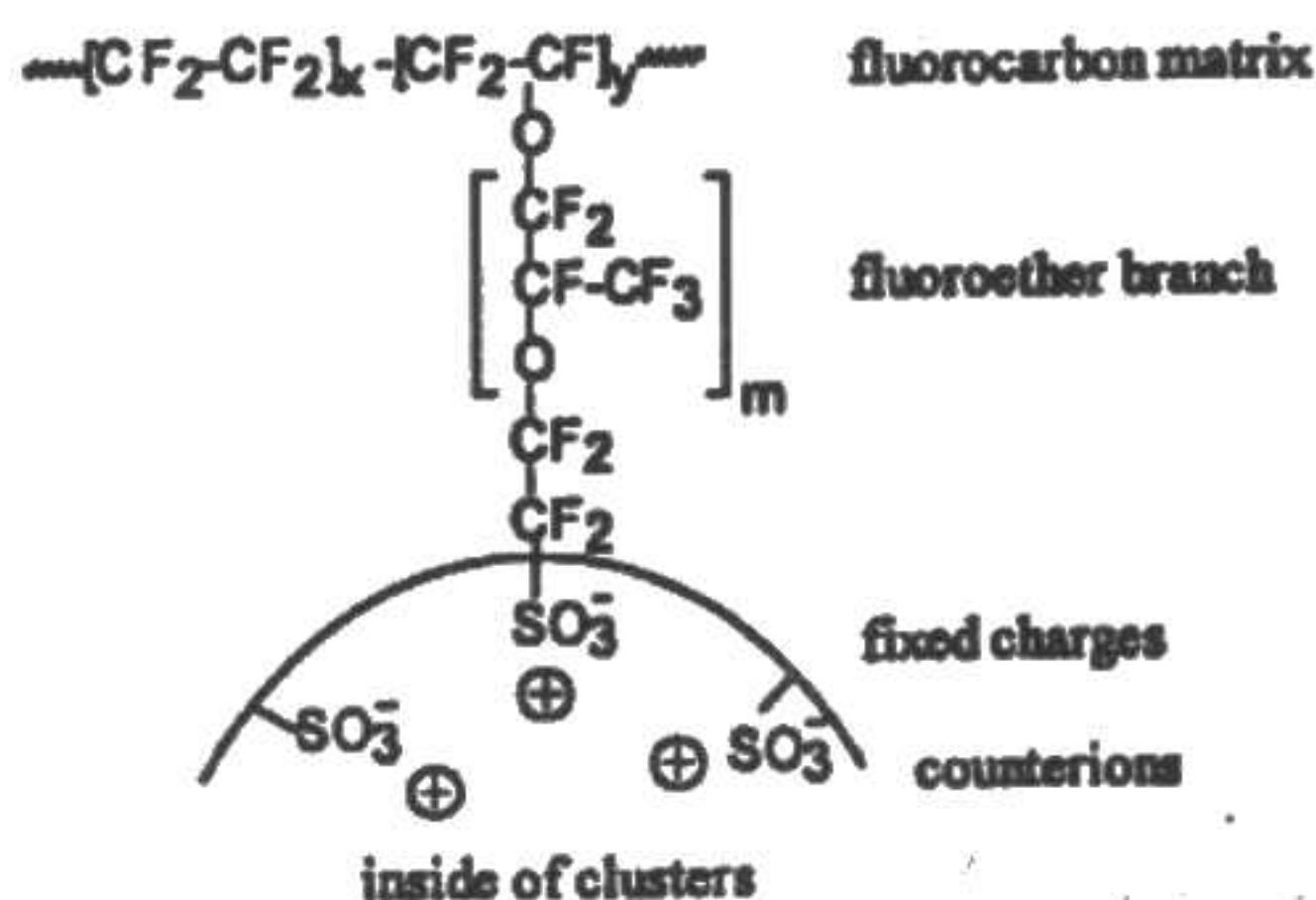


Figure 1. Schematic presentation of the regions of different polarity in a Nafion membranes.

Apparent transport number

The literature γ_{\pm} coefficients of NaCl in methanol solutions (see Fig. 2) when used for the calculation of the apparent transport number of Na^+ lead to irregular curve of $\bar{t}_{1,app}$ and even to $\bar{t}_{1,app} > 1$ (Fig. 3, $\gamma_{\pm}(m \leq 0.1)$ taken from [16], $\gamma_{\pm}(m > 0.1)$ – from [17]).

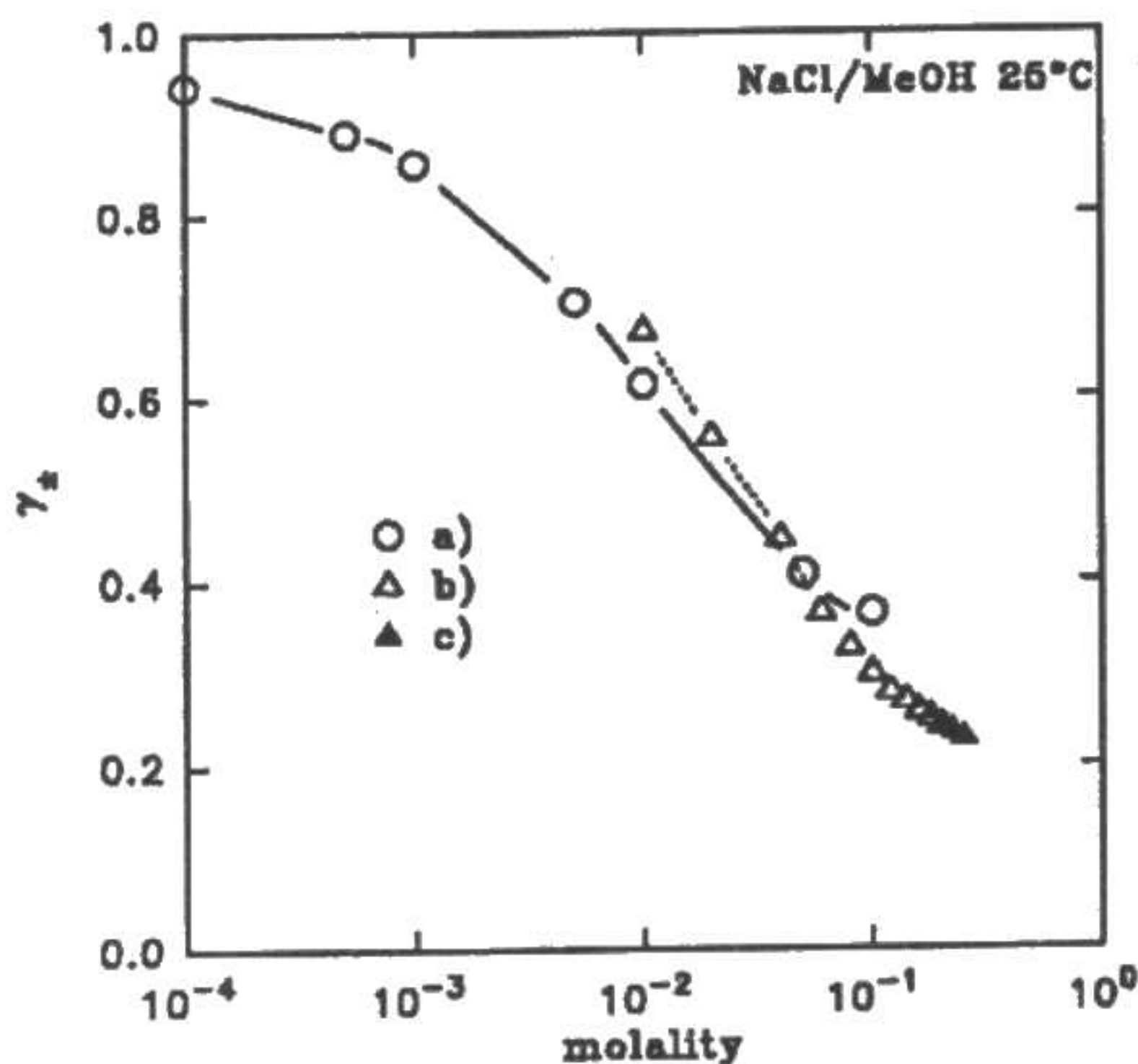


Figure 2. Mean activity coefficients in NaCl/MeOH at 25°C; a) Wolfenden *et al.* [16], b) Izmailov and Ivanova [17], c) Vlasov and Antonov [18].

Therefore to eliminate the uncertainty of the activity data, $\bar{t}_{1,app}$ was calculated taking the transport number of Na^+ , t_1 , in methanol NaCl solutions [15] and measuring the diffusion potential, ΔE_e , for the solutions of the same concentrations as those used for determining the membrane potential (eq. (7)).

$$\bar{t}_{1,app} = t_1 \frac{\Delta E}{\Delta E_e} \tag{7}$$

Calculated according to eq. (7) $\bar{t}_{1,app}$ never exceeds 1 (Fig. 3, open circles denoted by N117_{corr}).

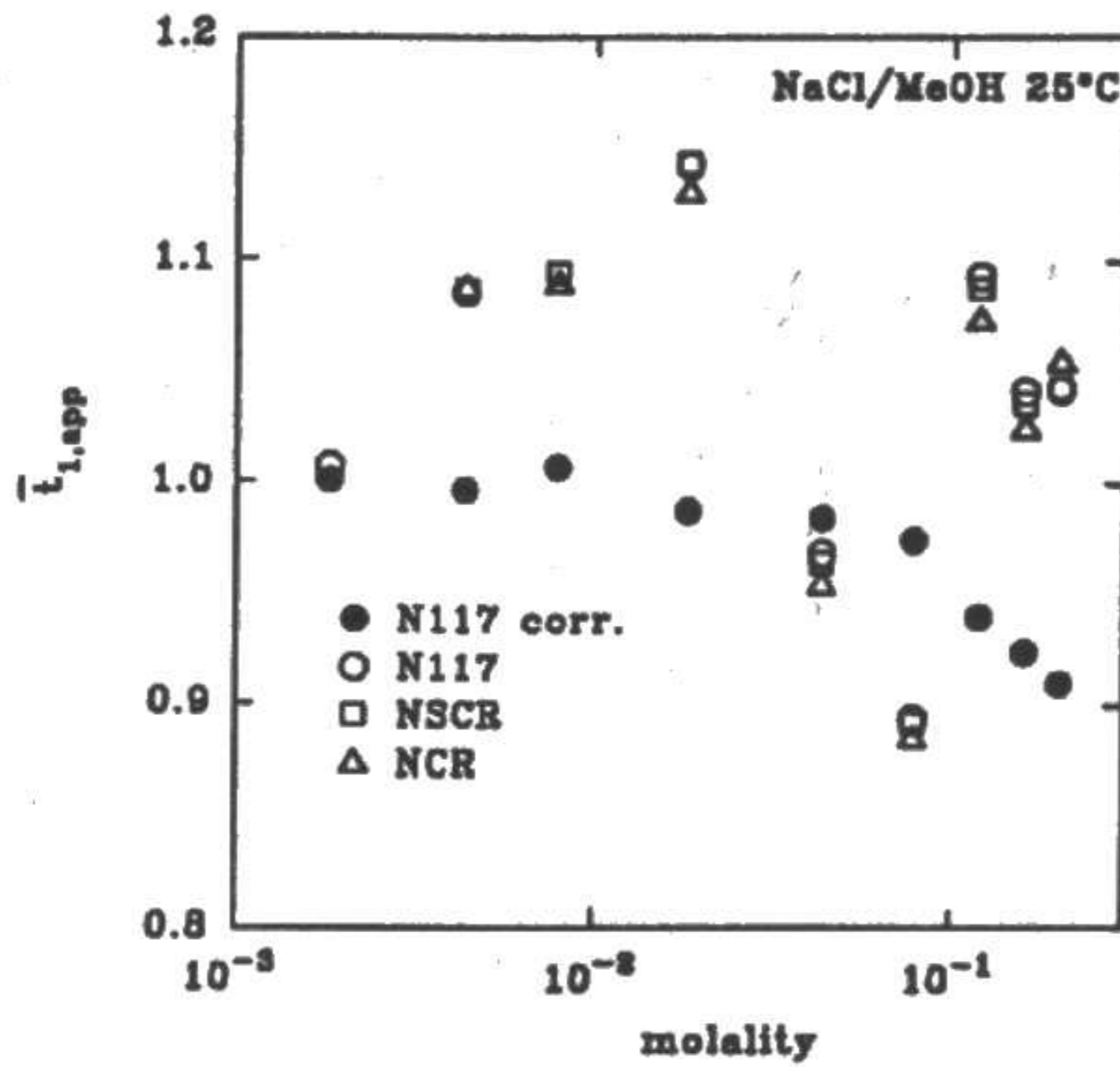


Figure 3. Apparent transport number of Na⁺ in Nafion membranes calculated from: eq. (2) – empty symbols, eq.(7) – filled circles (N117_{corr}).

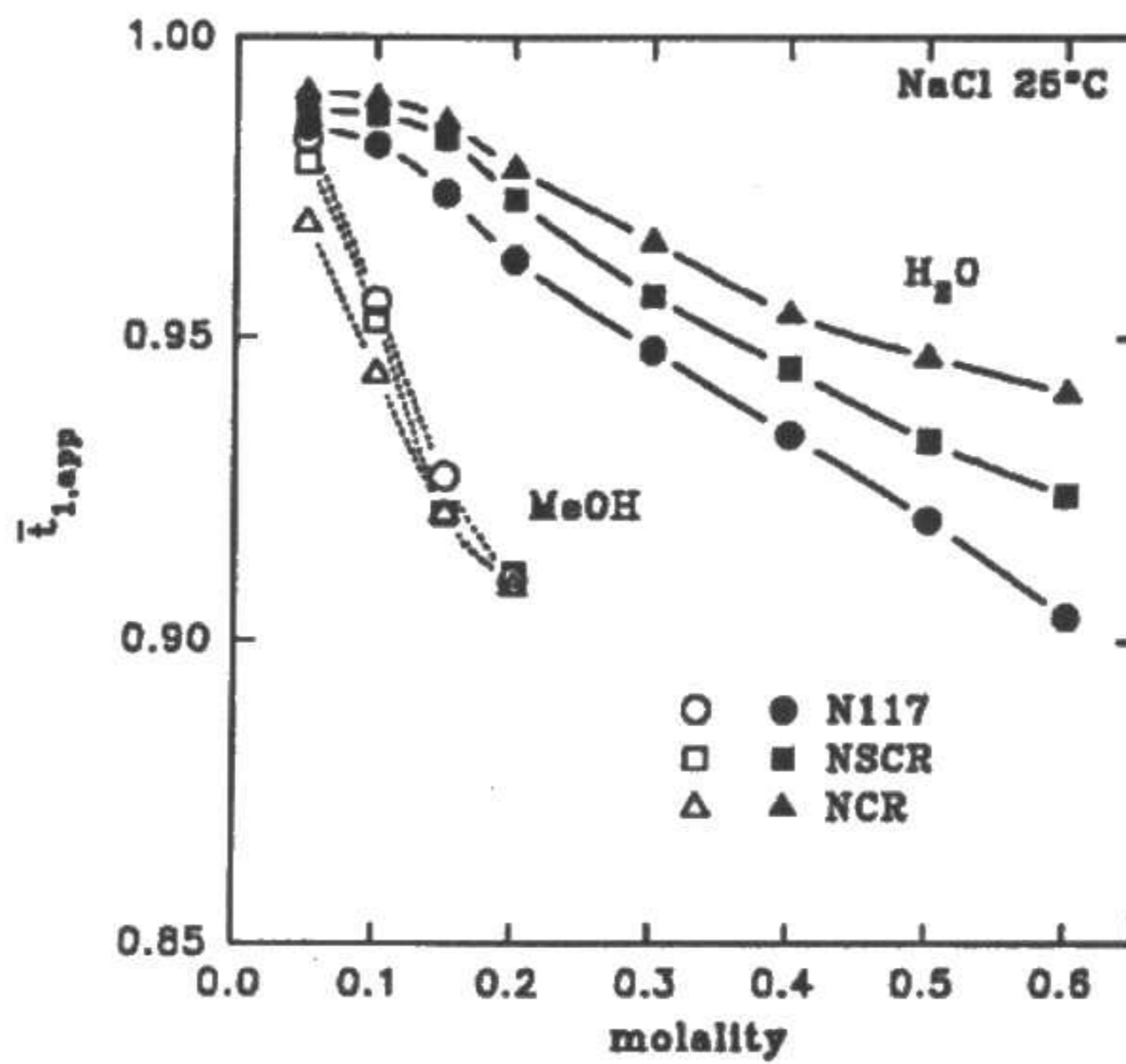


Figure 4. Apparent transport number of Na⁺ in Nafion membranes in methanol and aqueous solutions of NaCl; 25°C.

The general tendency observed in Fig. 4 is that apparent transport number of Na^+ is lower in MeOH solutions. Bearing in mind the physical meaning of $\bar{t}_{1,app}$ (eq. (8)):

$$\bar{t}_{1,app} = \bar{t}_1 - \frac{c_s}{c_0} \bar{t}_0 = \bar{t}_1 - M_0 m \bar{t}_0 \quad (8)$$

where \bar{t}_1 , \bar{t}_0 , M_0 , m are the real transport of ion i , the transport number of solvent, molecular mass of solvent, and molality, respectively, two factors can be indicated to reduce $\bar{t}_{1,app}$: lower \bar{t}_1 because of expected association of Na^+ with fixed charges, and/or higher second term in eq. (8) because of $M_{\text{MeOH}} > M_{\text{water}}$, if \bar{t}_0 of both solvents are comparable. To find which of these effects plays the dominant role, some preliminary measurements of electroosmotic transport of solvent in Nafion 117 were performed. It was found that the transport number of $\bar{t}_{\text{MeOH}} \approx 13 \text{ mol/F}$ whereas of water $-\bar{t}_{\text{water}} \approx 9 \text{ mol/F}$ in 0.2 m NaCl. Having calculated the term $M_0 m \bar{t}_0$ for both solvents (0.083, 0.032) it appears that the true transport numbers are close to each other and equal to ~ 0.98 . This fact would suggest that the ratios of the products of mobility and concentration of ions in the membrane, $\bar{c}_1 \bar{u}_1 / \bar{c}_2 \bar{u}_2$, in both solvents are similar. When discussing, however, the electric transport of associating electrolyte an additional factor should be considered – the possible dragging of neutral ion-pairs by the electroosmotic flow of solvent. Such phenomenon was observed and applied to the filtration of non-electrolytes by electroosmosis [21]. To quantify this effect let us start with the transport equations of linear non-equilibrium thermodynamics:

$$J_i = L_{i1} \Delta \tilde{\mu}_1 + L_{i2} \Delta \tilde{\mu}_2 + L_{i3} \Delta \mu_3 + L_{i0} \Delta \mu_0 \quad i = 1, 2, 3, 0 \quad (9)$$

where 1, 2, 3, 0 denote cation, anion, ion-pair, and solvent, respectively.

Remembering that for the thermodynamic equilibrium, $\tilde{\mu}_1 + \tilde{\mu}_2 = \mu_3 = \mu_s$, for the zero-current condition the following expression relating $\Delta E = \Delta \tilde{\mu}_2 / z_2 F$ and $\Delta \mu_s$ is obtained (electrolyte 1:1, compare eq. (10) with (8)):

$$\bar{t}_{1,app} = -\frac{F \Delta E}{\Delta \mu_s} = \bar{t}_1 - \frac{c_s}{c_0} \bar{t}_0 + \bar{t}_3 \quad (10)$$

where \bar{t}_3 is the transport number of neutral ion-pair, defined as:

$$\bar{t}_3 = \frac{L_{13} - L_{23}}{L_{11} - 2L_{12} + L_{22}} = \left(\frac{FJ_3}{I} \right)_{\Delta c, \Delta p = 0} \quad (11)$$

As the electroosmotic flow of the solvent is caused by moving counterions, the direction of flow of ion-pairs, expressed by \bar{t}_3 , will be the same as that of counterions, thus increasing their transport number. This effect should be proportional to the concentration of ion-pairs, *i.e.* to the concentration of sorbed electrolyte, and to the electroosmotic flow of the solvent. That is, if $\bar{c}_s \rightarrow 0$ \bar{t}_3 should go to zero, whereby

with increasing \bar{c}_s it should increase. On the other hand the higher sorption of electrolyte decreases the real transport number of counterions, the electroosmotic flow of solvent and, consequently, the transference of ion-pairs. The other observed feature is that, in contact with methanol solutions, the transport number of cations is higher in the membrane with sulfonic groups, whereas for the aqueous solutions - in the membrane with carboxylic groups. The $\bar{t}_{l,app}$ of Na^+ in the NSCR membrane with both kinds of groups is always between those two. It should be related to the significant increase of swelling of the carboxylate membrane when going from water to methanol. Another reason should be the difference in association of $\text{R-COO}^- - \text{Na}^+$ and $\text{R-SO}_3^- - \text{Na}^+$.

Conductivity

The specific conductivity of membranes in MeOH solutions is about half of that in aqueous solutions because of stronger association of ions in methanol (Fig. 5). This can be supported by the fact that the limiting conductivities of ions in both solvents are close one to another, whereas the association constants differ significantly (Table 2).

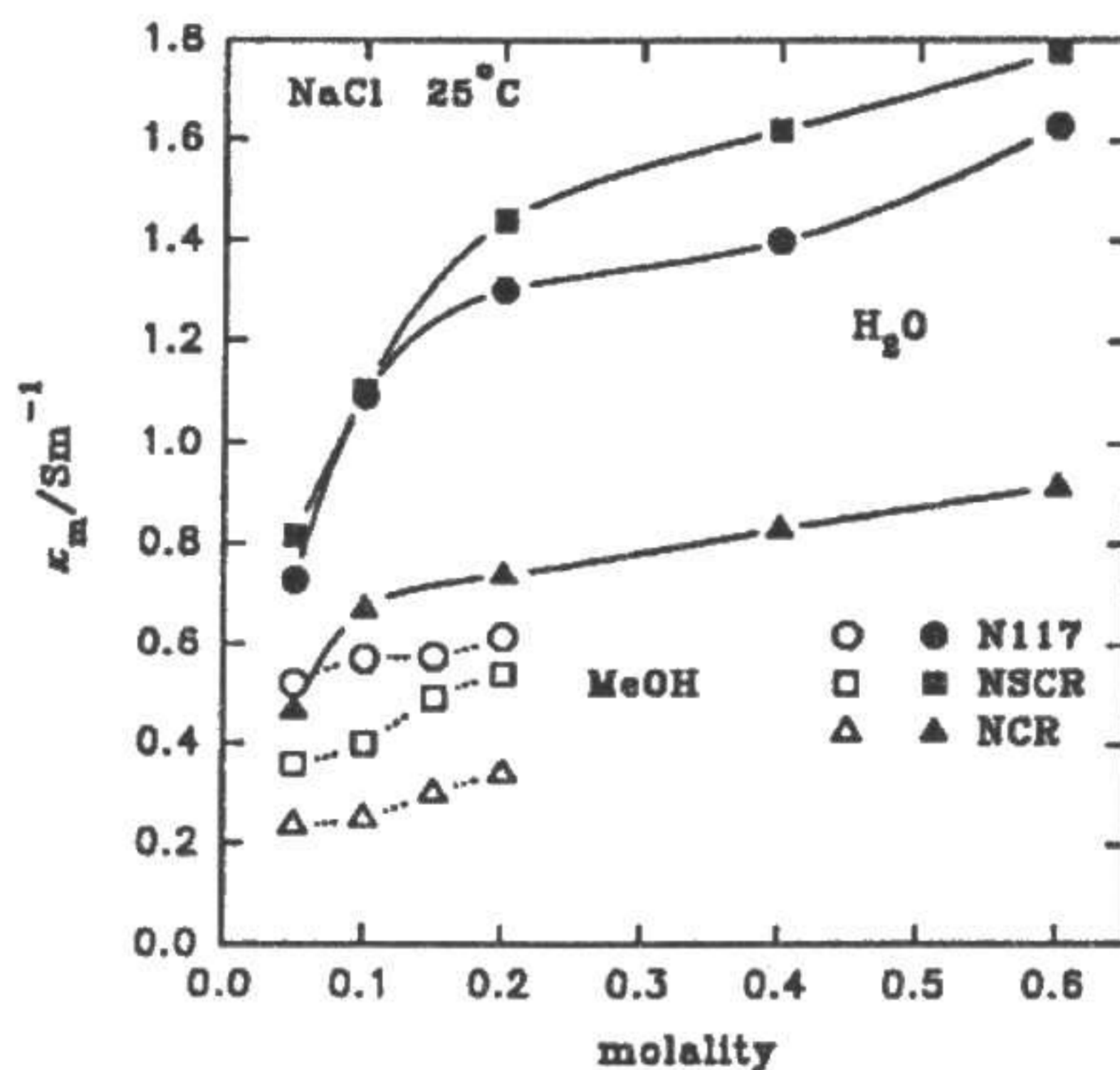


Figure 5. The specific conductance of Nafion membranes in methanol and aqueous solutions of NaCl; 25°C.

The differences in membrane conductivities when going from water to methanol solutions are similar to those of free solutions. These are 0.8 S/m in methanol and 2.0 S/m in water for 0.2 m NaCl. The ratio $0.8/2.0 = 0.4$ is similar to the corresponding ratio for membranes (see Table 2).

Table 2. The limiting conductivities of ions, λ_{∞} , and the association constant of NaCl, K_A , in methanol and aqueous solutions (25°C).

solution of NaCl	λ_{∞} [15] [$\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$]		K_A [22] [$\text{dm}^3 \text{mol}^{-1}$]
	Na^+	Cl^-	
MeOH	45.22	52.38	23.04
H ₂ O	50.10	76.35	1.80

Permeability of electrolyte and solvent (Figs. 6, 7)

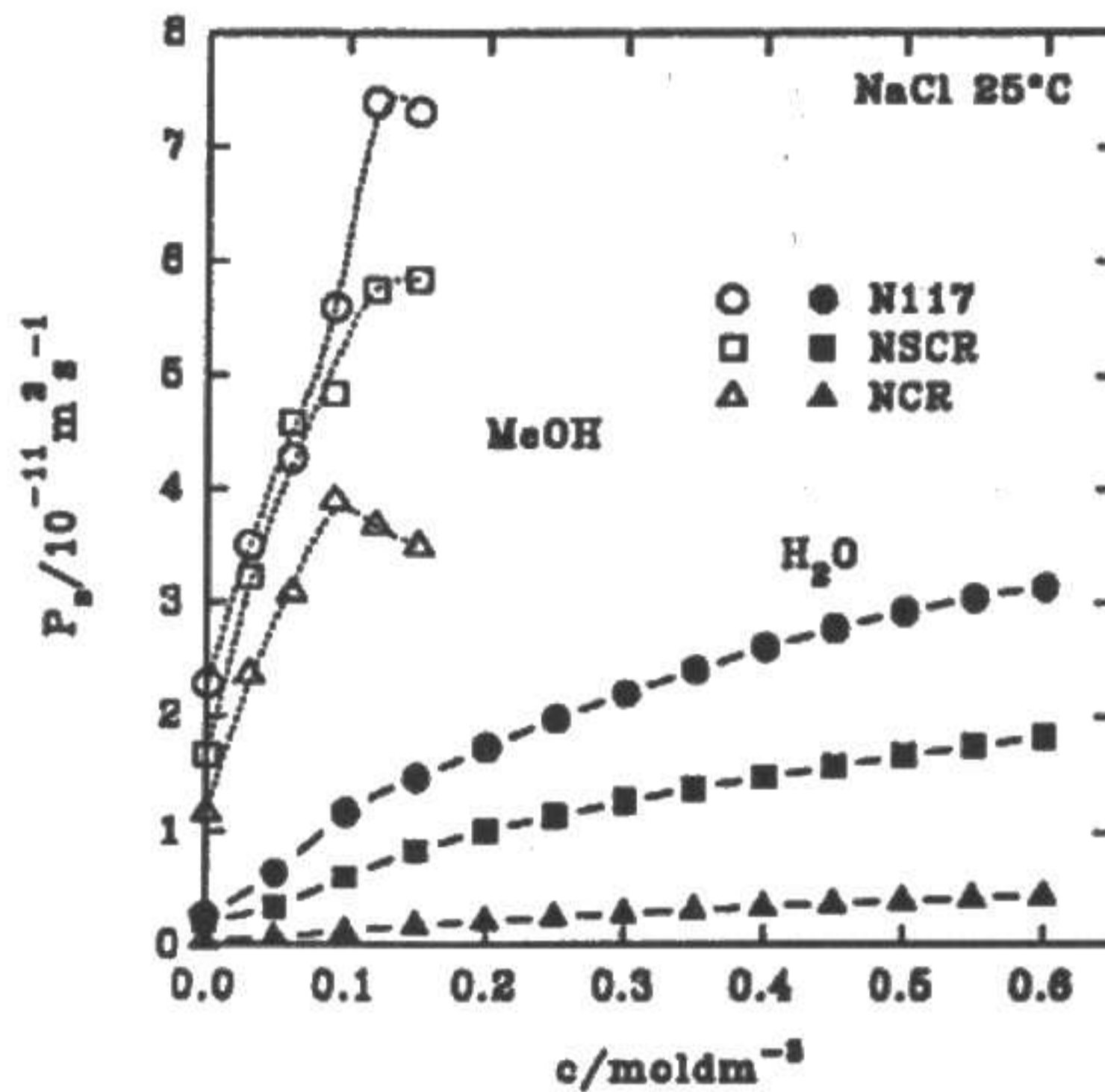


Figure 6. Permeability of NaCl in Nafion membranes in methanol and aqueous solutions; 25°C.

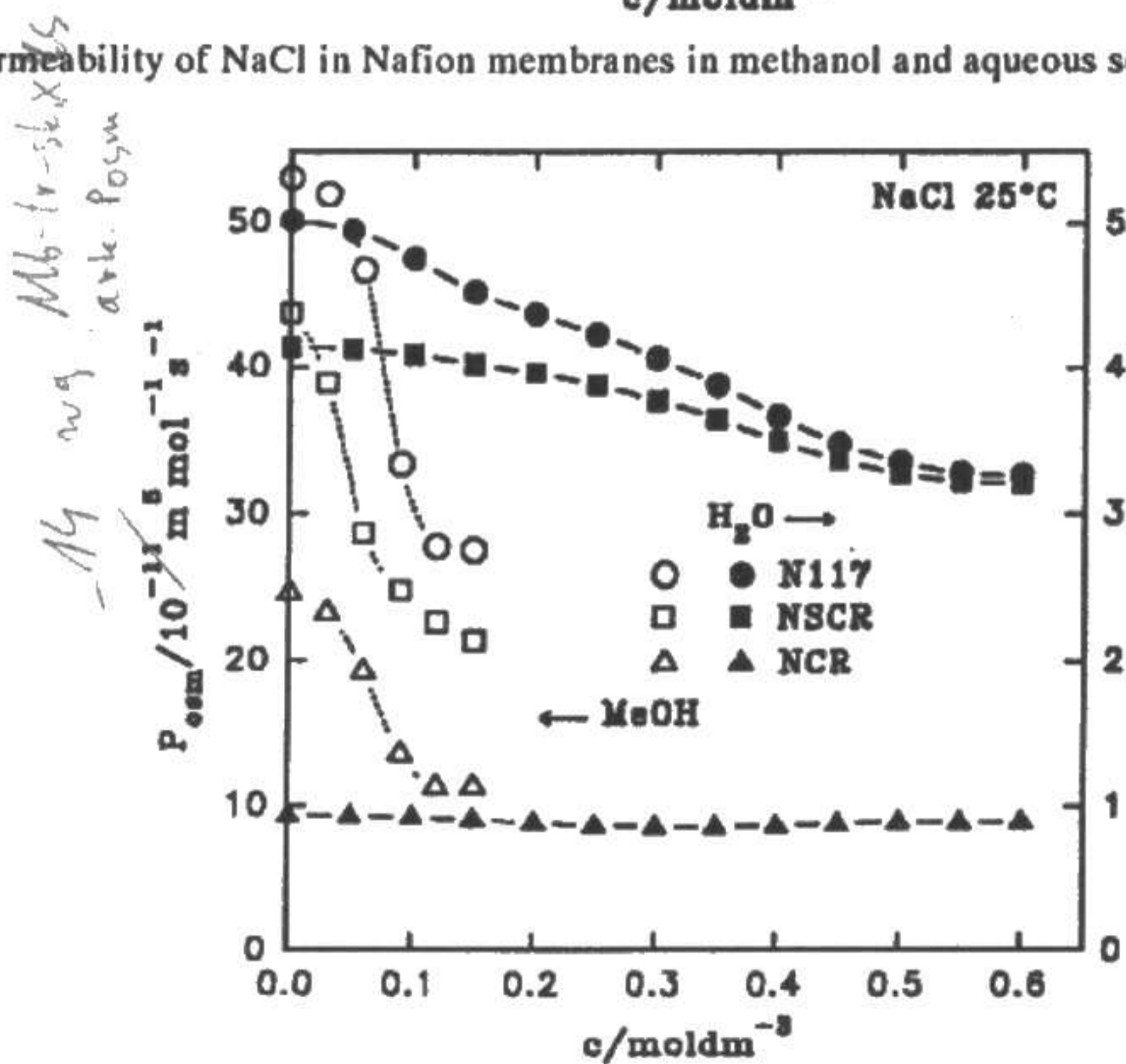


Figure 7. Osmotic permeability coefficient for Nafion membranes in methanol and aqueous solutions; 25°C.

When discussing the transport of particles across membranes the factor called tortuosity should be taken into account. It describes the elongation of path in a membrane due to the presence of a polymer matrix. The diffusion coefficient of salt in the solution filling the pores of the membrane, denoted as $\bar{D}_s^{(p)}$, and the diffusion coefficient in respect to the total volume of the membrane, \bar{D}_s , are related with the tortuosity factor, θ by (12) [23]:

$$\bar{D}_s = \bar{D}_s^{(p)} / \theta^2 \quad (12)$$

To present this effect in both solvents, the ratio of θ^2 have been calculated and is compared with the ratios of transport coefficients for 0.1 m NaCl (Table 3). For the estimation of θ the expression of Mackie and Meares [23] has been used:

$$\theta = \frac{1 + V_p}{1 - V_p} \quad (13)$$

Table 3. Ratio of transport coefficients in methanol and aqueous 0.1 M NaCl solutions and of tortuosity coefficient, θ , of membranes in pure solvents.

Membrane	$\frac{\kappa_m(\text{MeOH})}{\kappa_m(\text{H}_2\text{O})}$	$\frac{P_s(\text{MeOH})}{P_s(\text{H}_2\text{O})}$	$\frac{P_{\text{osm}}(\text{MeOH})}{P_{\text{osm}}(\text{H}_2\text{O})}$	$\left(\frac{\theta(\text{MeOH})}{\theta(\text{H}_2\text{O})}\right)^{-2}$
N117	0.53	5.5	6.6	6.9
NSCR	0.41	8.5	5.9	6.2
NCR	0.40	30.7	13.9	14.6

The volume fraction of polymer in the swollen membrane, V_p , has been calculated from the density of the dry membrane and the volume of solvents in the membrane taking their partial volumes from [9]. Before comparing the ratios of P_s and θ (Table 3) it should be noted that P_s is equal to \bar{D}_s multiplied by the partition coefficient K_s ((14)).

$$P_s = \bar{D}_s \frac{\bar{c}_s}{c_s} = \bar{D}_s K_s \quad (14)$$

Consequently the combination of (12, 14) gives:

$$\frac{P_s(\text{MeOH})}{P_s(\text{H}_2\text{O})} = \frac{\bar{D}_s^{(p)} K_s(\text{MeOH})}{\bar{D}_s^{(p)} K_s(\text{H}_2\text{O})} \left(\frac{\theta(\text{MeOH})}{\theta(\text{H}_2\text{O})}\right)^{-2} \quad (15)$$

The ratio of $\bar{D}_s^{(p)}$, evaluated by the Nernst-Hartley equation and the limiting ion conductivities (Table 2), equals 0.80. Comparing the permeability coefficient of NaCl, P_s , with θ for the studied membranes the similarity is observed, although the discrepancy for the carboxylate NCR membrane is striking. This again should be

attributed to the stronger association of counterions with carboxylic groups comparing to the sulfonic groups, when going from water to methanol. Thus, the partition coefficient, K_s , and consequently P_s should increase more for the NCR membrane than for membranes containing sulfonic groups. It should be noted that the comparison of thermodynamic permeability coefficient, L , instead of P , which are related by (16)

$$P = L \frac{\partial \mu_s}{\partial c_s} \quad (16)$$

does not change the conclusions, because the concentration derivative of the chemical potential of salt, $\partial \mu_s / \partial c_s$, in MeOH is close to that in water (0.1 M NaCl: 46.1 and 45.8 Jm³/mol², respectively). The equation similar to (15) can be applied also to the solvents. In that case the K_{solv} ratio should be close to one, because in both phases the solvents are in excess as compared to the salt. Thus, the observed accordance of the ratio of P_{osm} with that of θ would be expected if $\bar{D}_{solv}^{(p)}$ were comparable for methanol and water. Assuming, however, that $\bar{D}_{solv}^{(p)}$ is inversely proportional to the solvent viscosity (MeOH – 0.59 cps, water – 1.0 cps), the accordance is not so good. Comparing the concentration dependence of P_s and P_{osm} in methanol solutions a strong correlation is observed (Fig. 8a). The salt permeability, P_s , strongly increases with the concentration because of a high sorption and association of ions. It means that the ability of the membrane to reflect the salt decreases. Consequently the flow of methanol should also decrease, as it is observed. This effect in water in the same concentration range is small (Fig. 8b) as compared to methanol.

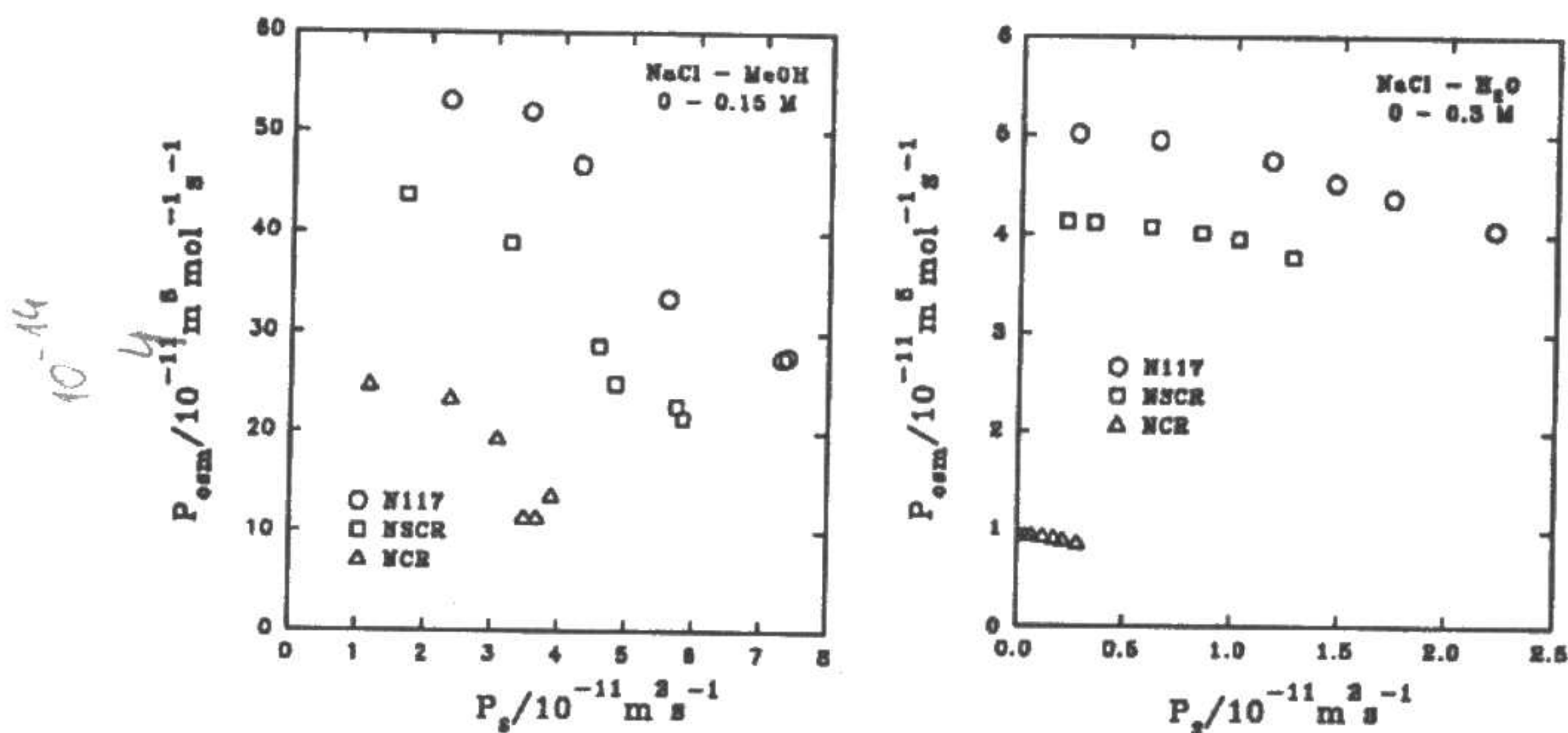


Figure 8. Relationship between osmotic, P_{osm} , and electrolyte, P_s , permeability coefficients for Nafion membranes in methanol (a) and aqueous (b) solutions of NaCl.

Conclusions

1. Nafion membranes are stable in methanol.
2. Because of a high swelling of membranes in methanol resulting in an extension of the channels the transport properties of Nafion membranes are not as good as in water and a lower electric conductance of membranes, higher diffusion of NaCl and osmotic flow of the solvent is observed. The properties of membranes are strongly related to the differences in the properties of solvents.
3. The decrease of separating ability of membranes is caused mainly by the increase of methanol and salt permeability; the transport numbers of Na⁺ counterions in both solvents are comparable.
4. From the point of view of the application in electrochemical devices, the largest decrease in the separating ability is observed for the membrane with carboxylic groups (NCR).

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