MODELLING OF NANOFILTRATION IN SOFTENING WATER

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Abstract

In this work, the results of membrane filtration of natural water together with theoretical description (modelling) are presented. The obtained results were described in terms of the semi–empirical mass transport models and the extended Nernst–Planck equation. The model of NF based on that equation, taking into account membrane structural parameters and ionic composition of waters, effective for ternary systems, in the case of real multionic solutions (with 8 ions) needs further improvement.

Key words: water treatment, nanofiltration, water softening, modelling

Introduction

Nowadays, the depletion of drinking water resources is increasing and therefore apart from surface springs, water for industrial and domestic purposes is also taken from deep wells.

Well water is usually characterized by high hardness. The quality of produced drinking water is determined by the Minister of Health in Regulation No. 203 dated 19.11.2002 point 1718 and by the Instruction of European Union no 98/83/EC dated 03.11.1998. Over the last years water treatment has been carried out applying effective and economic membrane techniques, which are an alternative to the traditional ones. Selection of optimum operating parameters and suitable membranes provides the basis for obtaining satisfactory effects in respect of drinking water production. Minimization of costs borne to initially test the membranes and set operating conditions for a system is feasible if appropriate mathematical models are applied. While using mathematical descriptions of membrane processes, the best effects are achieved by giving up generalizations and including the results of laboratory tests. Analyzing the overall nature of nanofiltration, one should take into account both efficiency and effectiveness.

Up to our knowledge, till now the existing transport models have been applied more or less satisfactorily to the description of real systems consisting of 3 kinds of ions [i,ii,iii,iv,v,vi]. In this work we apply the model based on the extended Nernst-Planck equation to the description of NF of natural waters containing at least 8 ions, to check its suitability for predictive purposes.

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Theory

The model system is as follows: feed containing n ions | polarisation layer | membrane | permeate.

Herein the term "membrane" is understood as that part of real membrane, which determines its transport properties. The membrane pores can be charged. Only the stationary state:

$$J_i(\text{polar.layer}) = J_i(\text{membrane}) \tag{1}$$

will be discussed. As the extended Nernst-Planck equation has been presented many times in the literature, here we present only the final equations for gradients of ion concentrations in the polarisation layer and in the membrane pore solution:

$$\frac{dc_i}{d\bar{x}} = J_v l_{pol} \left(\frac{c_i - c_{i,per}}{D_i} - z_i c_i \frac{\sum_{k=1}^{n} (c_k - c_{k,per})/D_k}{\sum_{k=1}^{n} z_k^2 c_k} \right) \quad i=1,..,n, \text{ polarisation layer} \tag{2a}$$

where $\bar{x} = x/l_{pol}$, and

$$\frac{d\bar{c}_i}{d\bar{x}} = J_v \frac{l_p}{X_p} \left(\frac{K_{c,i}\bar{c}_i - c_{i,per}}{\overline{D}_i} - z_i \bar{c}_i \frac{\sum_{k=1}^{n} (K_{c,k}\bar{c}_k - c_{k,per})/\overline{D}_k}{\sum_{k=1}^{n} z_k^2 \bar{c}_k} \right) \quad i=1,..,n, \text{ membrane} \tag{2b}$$

where $\bar{x} = x/l_p$, $\bar{x} \in \langle 0,1 \rangle$. In eqs.(2) the volume flux, J_v, refers to the unit area of membrane (not of pores), X_p is the area fraction of pores, l_p – their length, l_{pol} – thickness of polarisation layer. The ion concentrations are bounded by the electroneutrality condition:

$$\sum_i z_i c_i = 0 \text{ external solution} \tag{3a}$$

$$\sum_i z_i \bar{c}_i + X_m = 0 \text{ internal solution} \tag{3b}$$

where X_m is the volume density of fixed charges.

Usually it is assumed that the diffusion coefficient of ion i in the pore solution, $\overline{D}_i$, is related to D_i in the free solution by:

$$\overline{D}_i = K_{d,i} D_i \tag{4}$$

where $K_{d,i}$ is the diffusion hindrance factor which depends on $\lambda_i = r_i/r_p$ - the ratio of solute radius i, r_i, to the pore radius r_p - in the following manner [vii] (for $\lambda_i \leq 0.8$):

$$K_{d,i} = 1 - 2.3\lambda_i + 1.154\lambda_i^2 + 0.224\lambda_i^3 \tag{5}$$

Also the convection hindrance factor in eq.(2), $K_{c,i}$, depends on λ_i and on the kind of a membrane ($K_{c,i}$ can be >1 or <1). For our systems we haven't noticed any significant influence of that parameter on the model fitting; therefore we assume $K_{c,i}=1$ for all ions.

The boundary conditions for eqs.(2) are:

eq.(2a): $c_i(\bar{x}=0) = c_{i,f}$, $c_i(\bar{x}=1) = c_{i,f}^{(m)}$ \tag{6a}

eq.(2b): $\bar{c}_i(\bar{x}=0)=\bar{c}_i^{(m|f)}$, $\bar{c}_i(\bar{x}=1)=\bar{c}_i^{(m|per)}$ (6b)

Thus, the relation between the concentrations inside ($\bar{c}_i^{(m|f)}$, $\bar{c}_i^{(m|per)}$) and outside the membrane ($c_{i,f}^{(m)}$, $c_{i,per}$) has to be known. The partition of ions seems to be the crucial point of the model. In the description of the partition coefficient, apart from the Donnan potential, two terms should be taken into account – the steric one [ii, viii], $\Phi_{ster,i}$, and the term (denoted here as Φ_i) describing the specific ion interactions with membrane material [iv], and including solvation energy term resulting from the reduced dielectric constant of the pore solution [ix,viii]. Taking both terms into account, the ratio of the concentrations of ion i inside and outside the pore can be expressed as:

$$\frac{\bar{c}_i}{c_i} = \Phi_{ster,i}\exp\left(-z_i\frac{F}{RT}\Delta\psi_{Don}-\Phi_i\right) \quad i=1,..,n \tag{7}$$

where $\Delta\psi_{Don}=\bar{\psi}-\psi$ is the Donnan potential resulting from $X_m\neq0$. The steric term, $\Phi_{ster,i}$, depends on λ_i:

$$\Phi_{ster,i}=(1-\lambda_i)^2 \tag{8}$$

Eliminating $\Delta\psi_{Don}$ from (7), we obtain the following relationship used in the model calculations:

$$\bar{c}_1^{1/z_1}\bar{c}_i^{-1/z_i}=K_{D,1i}c_1^{1/z_1}c_i^{-1/z_i} \quad i=2,..,n \tag{9}$$

where

$$K_{D,1i}=\Phi_{ster,1}^{1/z_1}\Phi_{ster,i}^{-1/z_i}\exp(\Phi_i/z_i-\Phi_1/z_1) \tag{10}$$

Because of the complicated nature of Φ_i [iv], only the changes of solvation energy due to different dielectric constants of the pore, ε_p, and bulk (external), ε_b, solutions will be taken into account. According to [x, xi,viii,ix] Φ_i is equal:

$$\Phi_i=\frac{1}{RT}\frac{z_i^2 F^2}{8\pi N_A\varepsilon_0 r_i}\left(\frac{1}{\varepsilon_p}-\frac{1}{\varepsilon_b}\right) \tag{11}$$

where ε_0 – permittivity of vacuum, ε_b – dielectric constant of bulk solution, ε_p – dielectric constant of pore solution, N_A – Avogadro number.

To calculate Φ_i, we follow the work by Bowen and Welfoot [viii]. The radius of ion, r_i, will be taken as the hydrodynamic (Stokes) one, calculated from an ionic mobility. In order to calculate ε_p, these authors assumed that the wall of pore is covered with one layer of oriented water molecules of the thickness $d=0.28$ nm and of the dielectric constant ε_2 (the lowest value of ε_2 is given by the high frequency limit, $\varepsilon^*\approx6$), whereas the inner part of pore has the bulk properties ($\varepsilon_1=78.3$ - water). Then ε_p is calculated as the average (eq.(24) in [viii]):

$$\varepsilon_p = \frac{\int_0^{r_p-d} 2\pi r \varepsilon_1 dr + \int_{r_p-d}^{r_p} 2\pi r \varepsilon_2 dr}{\pi r_p^2} = \varepsilon_1 - 2(\varepsilon_1 - \varepsilon_2)(d/r_p) + (\varepsilon_1 - \varepsilon_2)(d/r_p)^2 \tag{12}$$

The unknown parameter l_p/X_p will be calculated from the experimentally measured volume flux of pure water, $J_{v,0}$, and the Hagen-Poiseuille equation which results in:

$$\frac{l_p}{X_p} = \frac{r_p^2}{8\eta_p}\left(-\frac{\Delta p}{J_{v,0}}\right) \tag{13}$$

Here $J_{v,0}$ refers to the unit area of membrane, $(-\Delta p/J_v)$ is determined experimentally. η_p is the viscosity of pore solution and is some combination of viscosity of the layer of oriented water molecules, η_2, and that of water filling the inner part of pore η_1. Bowen and Welfoot assumed that η_2, similarly to ε_p, is the area mean of η_1 and η_2 (eq.(14) in [viii]). However, it should be noticed that the volume flow through a pore of two regions of viscosity, inversely proportional to the average viscosity $V \propto r_p^4/\eta_p$, should be higher than that through the pore of radius (r_p-d) filled with the liquid of viscosity η_1. This inequality results in:

$$\frac{\eta_p}{\eta_1} < \left(\frac{r_p}{r_p - d}\right)^4 \tag{14}$$

As the area averaging (eq.(14) in [viii]) does not fulfil that inequality, we calculate the mean viscosity by averaging the linear velocity of water over the cross-section of pore:

$$\hat{v} = \frac{\int_0^{r_p-d} 2\pi r v_1 dr + \int_{r_p-d}^{r_p} 2\pi r v_2 dr}{\pi r_p^2} = \frac{r_p^2}{8\eta_p}\left(-\frac{\Delta p}{l_p}\right) \tag{15}$$

where v_1, v_2 denote the velocities in the pore regions of viscosities η_1 and η_2. v_i is obtained by solving the equation:

$$2\pi r \eta_i \frac{dv_i}{dr} = \frac{\Delta p}{l_p}\pi r^2 \qquad i=1,2 \tag{16}$$

in the appropriate boundary conditions, assuming that:

$$v_1 = v_2 = \left(\frac{r_p^2 - (r_p - d)^2}{4\eta_2}\right)\left(-\frac{\Delta p}{l_p}\right) \text{ at } r=r_p\text{-}d \tag{17}$$

The final formula for η_p is:

$$\eta_p = \left((1-y)^4/\eta_1 + y(4 - 6y + 4y^2 - y^3)/\eta_2\right)^{-1} \tag{18}$$

where $y = d/r_p$. Eq.(18) fulfils the inequality (14).

Calculations

Eqs. (2a) for polarisation layer have been solved for a given thickness l_p. The result - $c_i^{(m|f)}$ (eq.(6a)) – has been substituted into eq.(9) to yield $\bar{c}_i^{(m|f)}$ - the boundary condition (6b) for eqs. (2b). $c_{i,per}$ has been calculated from eq. (9), in which $\bar{c}_i^{(m|per)}$ obtained by solving eqs. (2b) has been substituted. The following function has been minimized using the simplex algorithm [xii]:

$$F = \sum_{i=1}^{n}\left(\left(c_{i,per,\text{model}} / c_{i,per,\text{exp}} - 1\right)^2 + \left(c_{i,per,\text{exp}} / c_{i,per,\text{model}} - 1\right)^2\right) \tag{19}$$

The second ratio, $c_{i,per,\text{exp}}/c_{i,per,\text{model}}$, has been added here to avoid $c_{i,per,\text{model}}$ going too close to zero. The values of model parameters (X_m, r_p, ε_p) have been also sought minimizing the deviations between the concentrations of ions in the polarisation layer, $c_{i,f}^{(m)}$, calculated from the membrane and polarisation layer sides.

Experimental

A membrane module produced by Osmonics Inc. and NF-membrane (DS-5-DK) were used. The experimental setup is shown in Fig. 1.
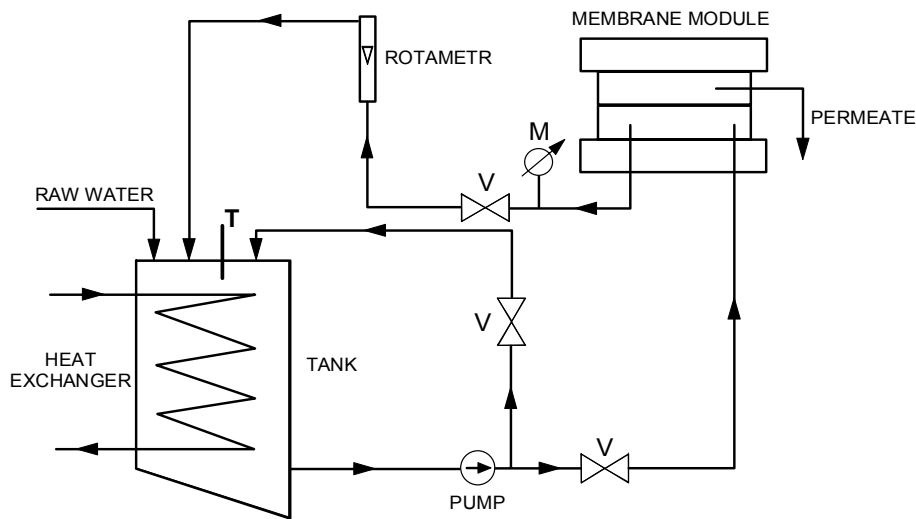

Fig. 1. Scheme of the pilot installation on a large-laboratory scale for the examination of membrane filtration.

The effective membrane area was 155 cm^2. Membrane filtration was carried out for 10 hours at constant process parameters, i.e. working pressure 1 and 2 MPa, flow over the membrane surface 1 m/s, medium temperature 25^{0}C. The initial feed volume was 10 litres. During the first 3 hours of membrane filtration, the permeate was transferred back into the feed tank to stabilize the volume flux (Jv) and ion concentration on both sides of the membrane. Then the concentration process was

carried out obtaining the permeate samples of 200ml and 500ml, the former being assayed for cation and anion concentrations.

The effectiveness of the membrane water treatment process was evaluated on the basis of the permeate flux. Physical and chemical analyses in the raw water and permeate were made. The concentration of magnesium and calcium, and determination of total hardness were carried out applying the complexometric titration with EDTA, while the concentration of chlorides was determined applying the titration by Mohr. Additionally the concentrations of ions by means of a chromatograph Dionex DX-120 and spectrometer Varian Spectr AA880 were assayed.

Two types of waters characterised by different total hardness (H_{tot}) were used in the experiment – a well water taken from Gliwice (H_{tot} over 700 mg $CaCO_3/dm^3$) and a tap water (H_{tot} over 400 mg $CaCO_3/dm^3$) for comparison.

Before the experiments with natural waters, the transport-separation characteristics of the tested membranes were determined using the solutions of NaCl and $MgSO_4$. Membrane effectiveness typical of NF was obtained during water filtration at pressures of 1 and 2MPs. Simultaneously, the efficiency of the process described as permeate flux was found to be $15 \cdot 10^{-6}$ $m^3/m^2 s$.

Determination of best estimates of ion concentrations

The concentrations of ions have been determined independently. Because of some errors in analysis, the concentrations usually fulfil neither the balance equation:

$$c_{i,1}V_1 = \sum_{k=2}^{m-1} c_{i,k}V_k + c_{i,m}V_m \qquad i=1,...,n \qquad (20)$$

nor the electroneutralty condition:

$$\sum_{i=1}^{n} c_{i,k}z_i = 0 \qquad k=1,..,m \qquad (21)$$

In the above equations, the subscript i denotes i-th ion, 1 – feed at the beginning of NF process, k – k-th sample of permeate (numbered from $k=2$ to $k=m$-1), m – feed at the end of NF process, V_k – volume of k-th sample.

In order to fulfil these balance equations, we have applied the Lagrange multiplier method [xiii]. Let us introduce the following notation:

$\eta_1 = c_{1,1}, \eta_2 = c_{1,2},...,\eta_m = c_{1,m}$,

$\eta_{m+1} = c_{2,1}, \eta_{m+2} = c_{2,2},...,\eta_{2m} = c_{2,m}$,

...

$\eta_{(n-1)m+1} = c_{n,1}, \eta_{(n-1)m+2} = c_{n,2},...,\eta_{nm} = c_{n,m}$

According to that method, the best estimate for the column vector $\boldsymbol{\eta}$ ($\eta_1,.., \eta_{nm}$) is given by the formula:

$$\tilde{\boldsymbol{\eta}} = \mathbf{y} - \mathbf{C}_y \mathbf{B}^T \left(\mathbf{B} \mathbf{C}_y \mathbf{B}^T \right)^{-1} \mathbf{B} \mathbf{y} \tag{22}$$

where $\mathbf{y}$ is the vector analogous to $\boldsymbol{\eta}$ but containing the measured values of $c_{i,k}$, $\mathbf{C}_y$ is the covariance matrix for $\mathbf{y}$; it is a diagonal matrix, because the measurements of concentrations are independent. The diagonal elements are squares of measurement errors. $\mathbf{B}$ is the matrix $(n+m)$ x nm, defined by eqs.(20), (21) which can generally be written as:

$$\sum_{k=1}^{nm} b_{ik} \eta_k = 0 \qquad i=1,...,n+m, \quad \text{or} \quad \mathbf{B}\boldsymbol{\eta} = 0 \tag{23}$$

Results and Discussion

l_p/X_p from the hydrodynamic flux of water

For $\Delta p=2$ MPa, the measured flux of water through DS-5-DK was $2.309 \cdot 10^{-5}$ m/s. These results, according to eq.(13), yield:

$$\frac{l_p}{X_p} = 1.083 \cdot 10^{10} \frac{r_p^2}{\eta_p} \tag{24}$$

This relation will be used in the model calculation of natural waters. The viscosity of pore solution, η_p, will be calculated from eq.(18), assuming that $\eta_1=0.00089$ N·s/m^2 (the viscosity of water at 298 K) and, similarly to [viii], that the viscosity of the layer of oriented water molecules, η_2, is ten times that of η_1.

Nanofiltration of single salts – 0.5% NaCl i 0.5% MgSO$_4$

The results for single salts are gathered in Table 1. The analysis of the retention coefficients of Cl$^-$ and Mg^{2+} ions obtained while testing the membranes with model solutions of the salts reveals the following effects concerning the removal of those ions for DS-5-DK (1MPs): R_{Cl} = 11.7%, R_{Mg} = 97.7%, and for DS-5-DK (2MPs): R_{Cl} = 12.4%, R_{Mg} = 98% (Tab.1). These results serve as a basis for naming the membranes tested as nanofiltration membranes due to the varied degree of monovalent and bivalent ions retention. Furthermore, it has been observed that the high values of the flow are typical of NaCl filtration and low values of the filtration of MgSO$_4$.

Table 1. Retention of 0.5% NaCl and 0.5% MgSO4 by DS-5-DK, $\Delta p=2$ MPa.

electrolyte	retention coeff. [%]	J_v [10^{-6} m/s]
0.5% NaCl	12.4	18
0.5% MgSO$_4$	98	12

In the case of binary electrolyte solutions, there is only one concentration of electrolyte which has to be fitted to the experimental one. Therefore, there are many values of model parameters giving full correspondence of model with the experimental data. To recognize what is the order of X_m, we have determined the apparent transport number of Na^+ in DS-5-DK by the emf method. The result - $\bar{t}_{+,app}$ =0.44 for the mean molality of external solution m=0.05 in comparison to t_+=0.388 in a free solution of that concentration – indicates a very small negative ($\bar{t}_{+,app}$ >t_+) charge of the order $10^{-1}.- 10^0$. Similar measurements for m=0.015 MgSO4 solution have yielded $\bar{t}_{+,app}$ =0.30, which indicates a small positive ($\bar{t}_{+,app}$ <t_+=0.40) charge of membrane. In Fig. 2 X_m versus l_{pol} for the model with $K_{D,1i}$ taking into account only the steric effect (eq.(10) reduced to $K_{D,1i} = \Phi_{ster,1}^{1/z_1}\Phi_{ster,i}^{-1/z_i}$) are presented. It is seen that for a given thickness of polarisation layer, l_{pol}, and radius of pores, r_p, two values of density of fixed charges, X_m, are possible – negative and positive one (because of higher mobility of anions, the concentration of negative fixed charges (dotted lines) is higher than that of positive
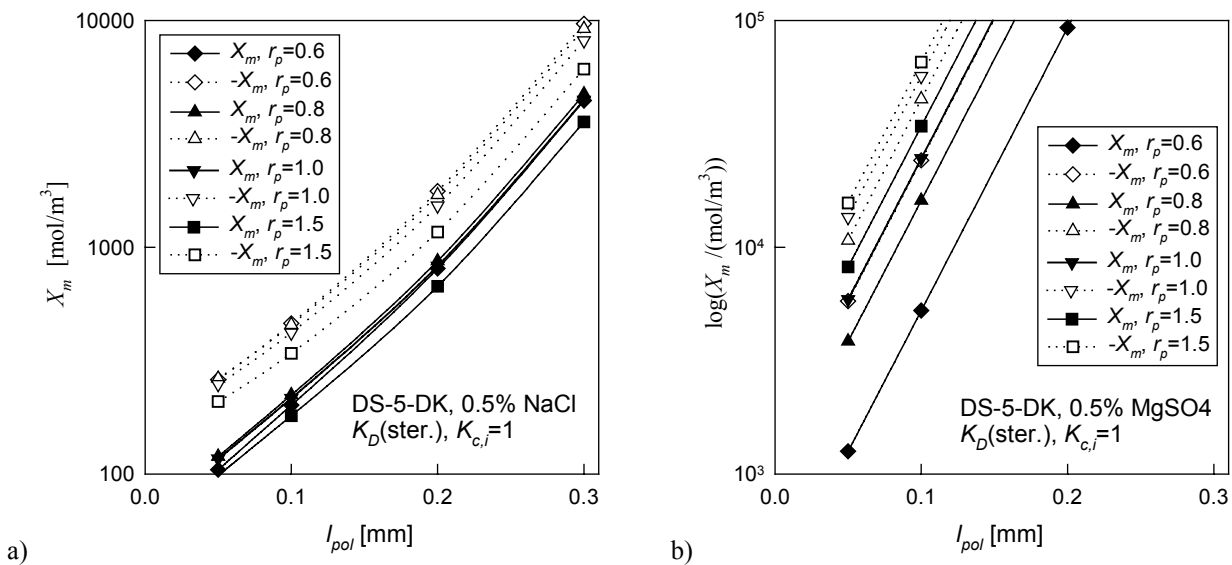

Fig. 2. Model with K_D depending on the steric effect only, $K_{c,i}$=1, viscosity as for water; a) DS-5-DK|0.5% NaCl, b) DS-5-DK|0.5% MgSO$_4$.

charges). X_m strongly depends on l_{pol} and even for the lowest reasonable value 0.1 mm it attains much too high values, especially in the case of MgSO$_4$ (Fig. 2b).

In **Fig. 3** the influence of dielectric constant and the viscosity on X_m is shown (for r_p=1 nm, $K_{c,i}$=1). Here X_m is calculated for the following variants:

1) K_D depends on the steric effect only and the viscosity of pore solution: a) equals that of water (K$_D$(ster.), η(H$_2$O)), b) is given by eq.(18) (K$_D$(ster.), η),

2) K_D depends on the steric effect and on the dielectric constant, given by (12) assuming that the dielectric constant of oriented water molecules near the pore walls is ε_2=31 (as suggested in [8]), and the viscosity of pore solution: a) equals that of water (K_D(ster.), $\eta(H_2O)$), b) is given by eq.(18) (K_D(ster.), η).
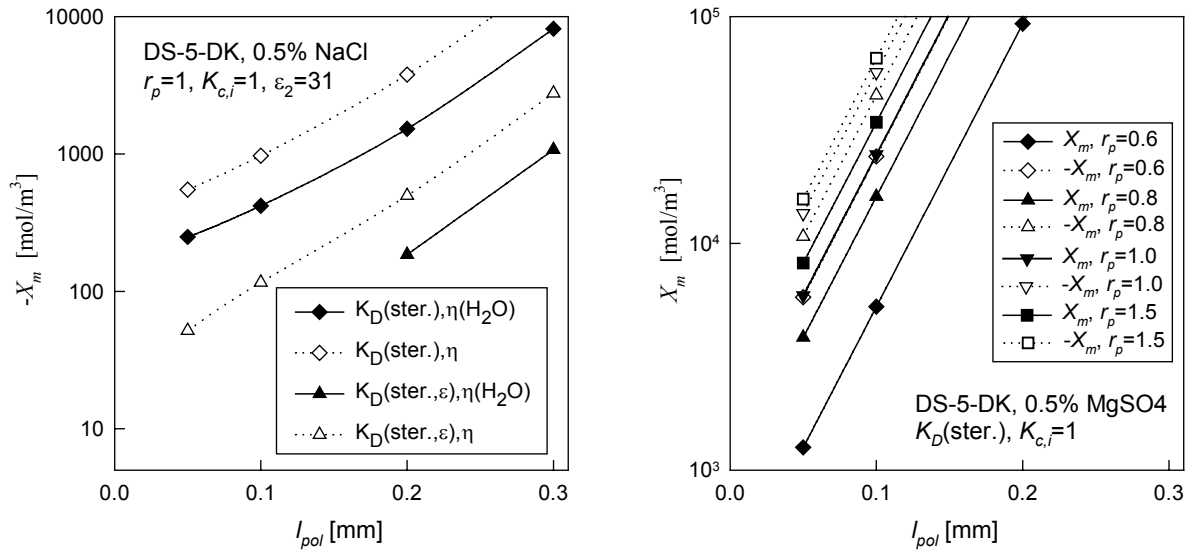

Fig. 3. Variants of model (see the text): a) DS-5-DK|0.5% NaCl, b) DS-5-DK|0.5% MgSO$_4$.

It is seen that:

1) the decrease of dielectric constant of the internal solution, ε_p, substantially decreases X_m which can be concluded from eqs.(7) and (11); still however X_m is high which indicates that the assumed ε_p and/or the pore radius is too high, assumed in those calculations (r_p=1 nm),

2) assuming higher viscosity, η_p, than that of water, what is justified, results in thinner and/or more porous membrane (l_p/X_p is inversely proportional to η_p, (eq.(13)) and thus to the increased fixed charge density X_m; fortunately this effect is much weaker than the dielectric one.

All the above calculations we have performed assuming for all ions the hindrance coefficient equal $K_{c,i}$=1. One can think that such high X_m for MgSO$_4$ results from that assumption. However, assuming that $K_{c,i}$ is given by [vii]:

$$K_{c,i} = 1 + 0.054\lambda_i - 0.988\lambda_i^2 + 0.441\lambda_i^3 \tag{25}$$

the calculated values of X_m are practically the same as for $K_{c,i}$=1 (Table 2).

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Table 2. DS-5-DK / 0.5%MgSO$_4$ − -X_m($K_{c,i}$=1) and the ratio X_m($K_{c,i}$≠1)/X_m($K_{c,i}$=1), model calculations with K_D, dielectric constant (ε_2=31), and viscosity given by eqs.(10), (12), and (18), respectively.

r_p [nm]	$K_{c,Mg}$2+	$K_{c,SO4}$2-	l_{pol}=0.1 mm		l_{pol}=0.2 mm		l_{pol}=0.3 mm	
			-X_m(K_c=1)	X_m(Kc≠)/X_m(Kc=1)	-X_m(K_c=1)	X_m(Kc≠)/X_m(Kc=1)	-X_m(K_c=1)	X_m(Kc≠)/X_m(Kc=1)
0.6	0.785	0.900	8.36	0.989	663	1.000	11800	1.000
0.8	0.873	0.944	527	0.991	9310	0.988	165000	0.987

Multiionic well waters

The ionic composition of waters, determined experimentally and their best estimate, is gathered in Table 3. The retention of all ions is shown in Fig. 4.

Table 3. Experimental concentrations of ions in feed and permeate [mol/m^3] and their best estimates (b.e.) calculated according to eq.(22).

|	Cl-	NO3-	SO42-	HCO3-	Na+	K+	Mg2+	Ca2+
				Gliwice, 1 MPa				
$c_{i,f,exp}$	14.87	0.184	4.67	6.36	11.79	0.326	2.61	7.60
$c_{i,per,exp}$	9.79	0.128	0.134	1.96	8.92	0.233	0.239	0.751
$c_{i,f}$ (b.e.)	15.50	0.179	4.80	5.49	11.36	0.310	2.56	7.00
$c_{i,per}$(b.e.)	8.96	0.128	0.134	1.93	9.06	0.234	0.240	0.762
				Gliwice, 2 MPa				
$c_{i,f,exp}$	15.37	0.186	4.62	6.24	11.93	0.331	2.64	7.64
$c_{i,per,exp}$	9.16	0.125	0.121	1.72	8.81	0.222	0.213	0.509
$c_{i,f}$ (b.e.)	15.74	0.182	4.70	5.46	11.16	0.322	2.59	7.06
$c_{i,per}$(b.e.)	8.78	0.125	0.121	1.72	9.19	0.223	0.214	0.512
				tap water, 2 MPa				
$c_{i,f,exp}$	1.92	0.124	1.58	4.97	1.31	0.100	1.32	3.69
$c_{i,per,exp}$	1.09	0.069	0.094	1.26	1.08	0.082	0.241	0.472
$c_{i,f}$ (b.e.)	1.96	0.122	1.63	4.83	1.27	0.099	1.27	3.13
$c_{i,per}$(b.e.)	1.08	0.070	0.094	1.25	1.08	0.082	0.242	0.475
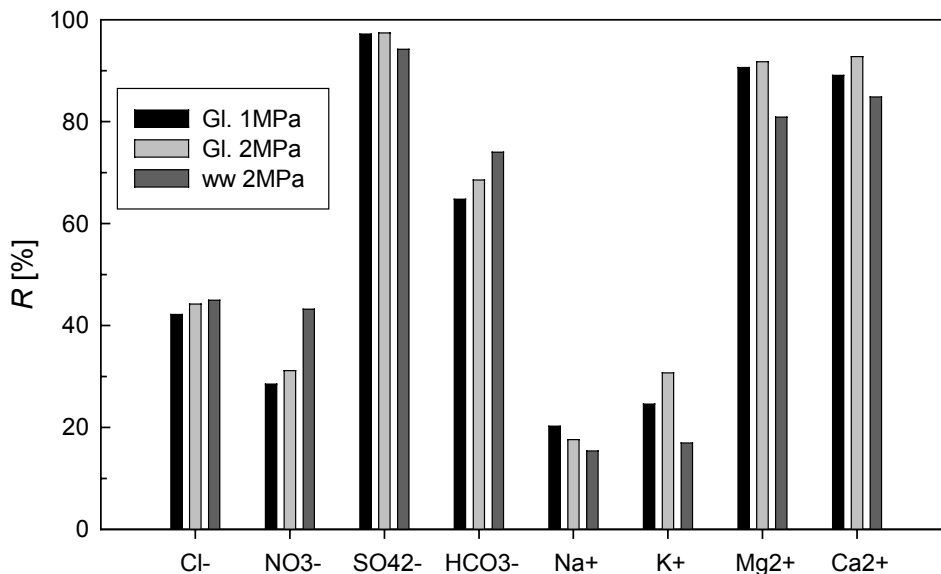
Fig. 4. Retention coefficient of ions, DS-5-DK membrane, Gliwice 1 MPa, Gliwice 2 MPa and tap water (ww) 2 Mpa.

It is seen that lower retention of Mg^{2+} ions ($R \approx 90\%$ for well water from Gliwice, $R \approx 80\%$ for tap water), and higher R of Cl^- ions ($R > 40\%$) have been obtained during the process of membrane softening of natural waters in comparison to the results of single electrolyte solutions (Tab.1). This is due to the multicomponent nature of the examined waters as well as different concentrations of the ions in the treated waters and model solutions of the salts.

Below we present results for 2 variants of the model. Both are based on: $K_{c,i}=1$, $K_{d,i}$, $K_{D,1i}$, η_p given by eqs.(5), (10), (18). They differ in the estimation of ε_p – in the 1st variant ε_p is calculated from eq.(12) assuming $\varepsilon_2=6$, in the 2nd variant ε_p is independent fitting parameter. Because of poor results obtained for binary electrolyte solutions as well as for multiionic waters, the variant with $K_{D,1i}$, depending on the steric effect only, is not presented here.
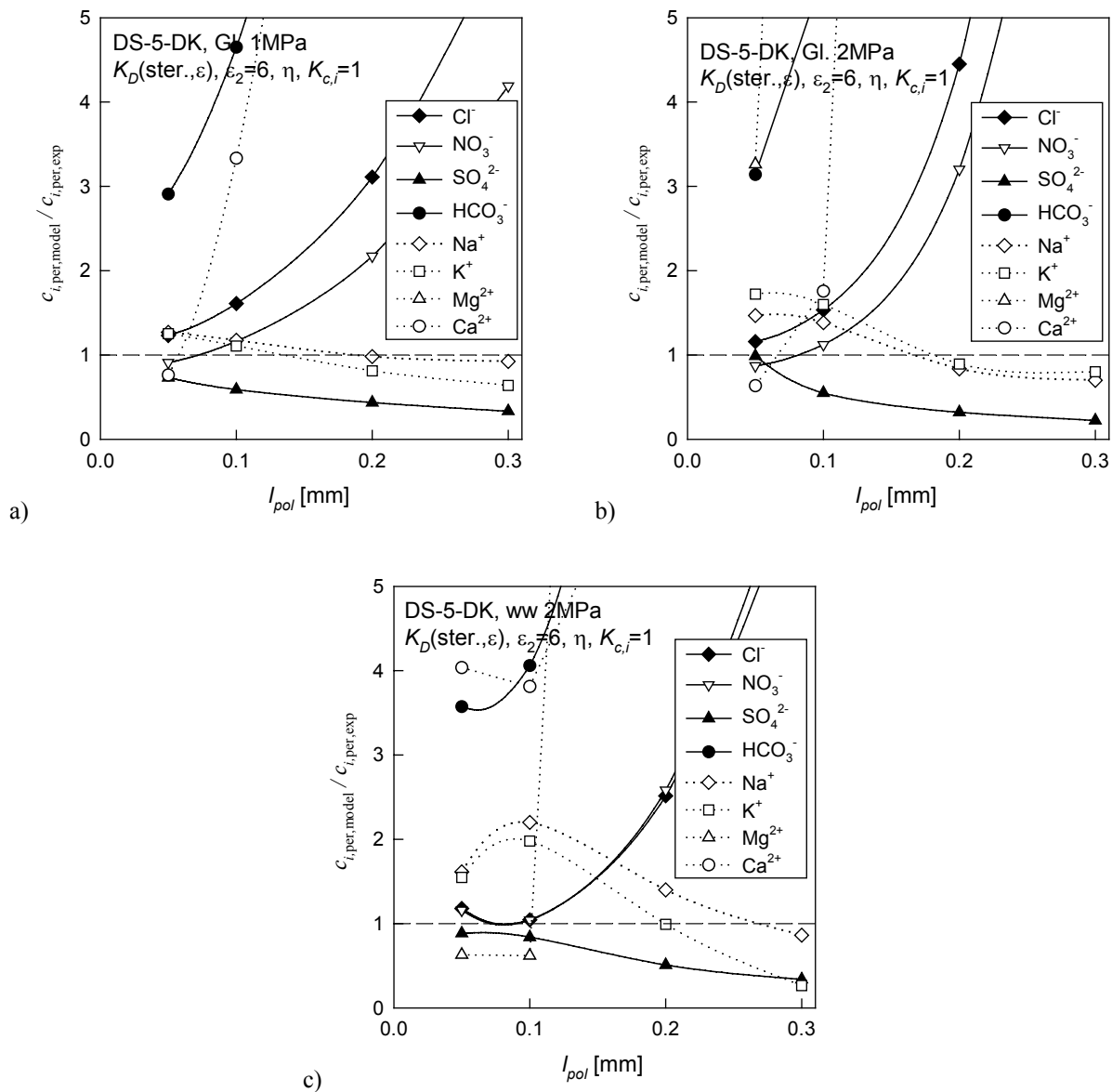

Fig. 5. Ratio of $c_{i,per,model}/c_{i,per,exp.}$ vs l_{pol}, model with K_D, ε_p ($\varepsilon_2=6$), η_p given by eqs.(10),(12), (18), respectively; membrane DS-5-DK, a) Gliwice 1 MPa, b) Gliwice 2 MPa, c) tap water 2 Mpa.
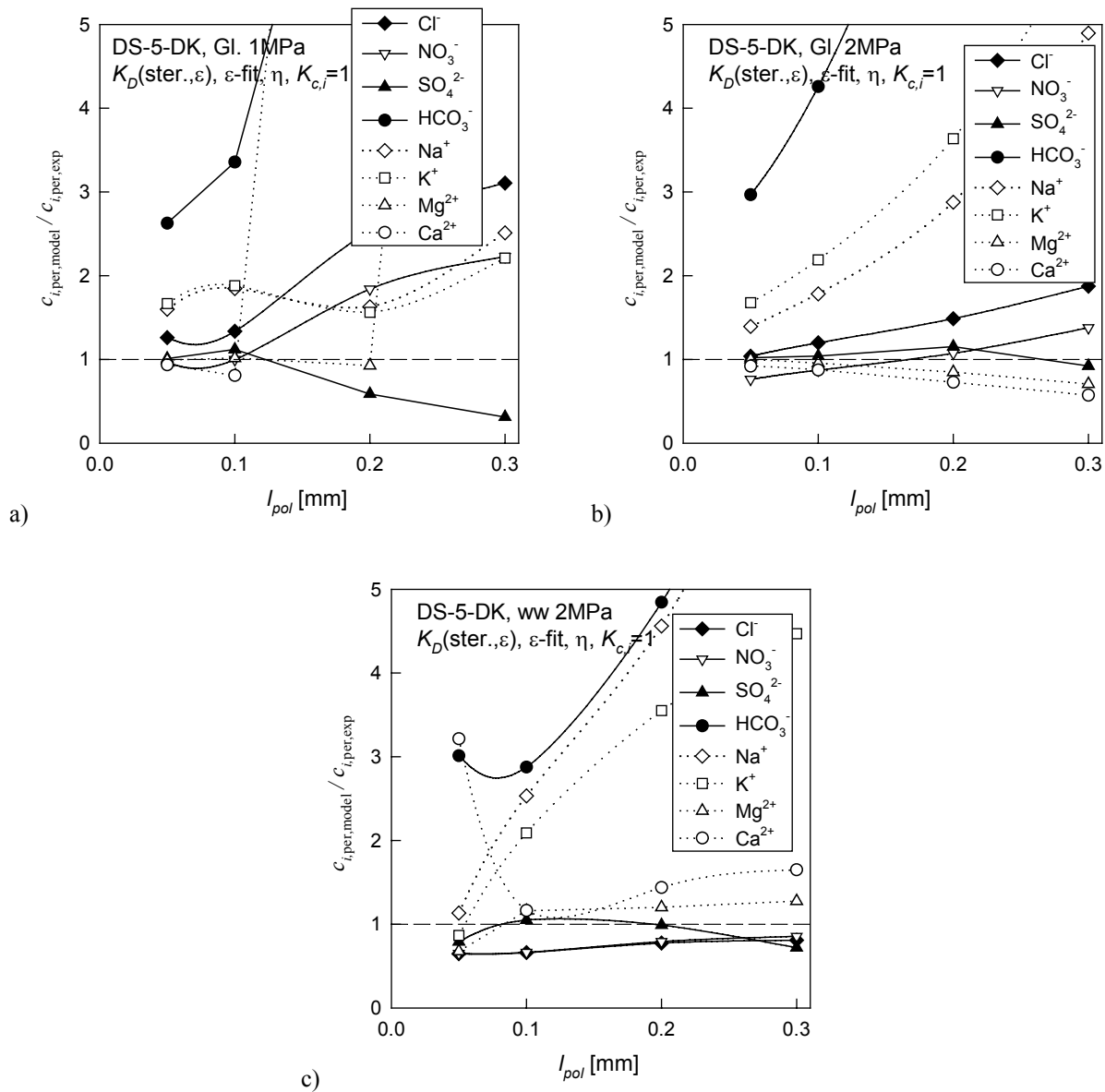
Fig. 6. Ratio of $c_{i,per,model}/c_{i,per,exp.}$ vs l_{pol}, model with K_D , η_p given by eqs.(10), (12), respectively; dielectric constant of pore solution is fitted; membrane DS-5-DK, a) Gliwice 1 MPa, b) Gliwice 2 MPa, c) tap water 2 Mpa.

Analysing the results shown in **Fig. 5** and **Fig. 6** one can see that the model cannot be successfully fitted to the experimental data concerning real multiionic waters In the case of variant 1 the best fitting has been achieved in the case of univalent cations Na^+ and K^+ , wheras the worst one for divalent cations Ca^{2+} and Mg^{2+} and for anion HCO_3^- (**Fig. 5**). If the dielectric constant of pore solution is a fitting parameter (variant 2, **Fig. 6**), then the situation is opposite. We observe the best agreement for divalent cation Mg^{2+}, not so good for Ca^{2+}, and much worse for univalent cations Na^+ and K^+. Regarding the anions the best fit is also observed for divalent ion SO_4^{2-}. Generally, the variant 2 gives better results than the variant 1, however also in this case the concentration of HCO_3^- in permeate is significantly overestimated.

As far as the ratio between ion concentrations in the polarisation layer is concerned $c^{(m)}_{i,f,m} / c^{(m)}_{i,f,pol}$, where $c^{(m)}_{i,f,pol}$ denotes concentration calculated from the experimental concentration of ion in the feed for a given l_{pol}, $c^{(m)}_{i,f,m}$ and is the concentration calculated from the membrane model and from $c_{i,per,exp}$, we must conclude it looks a bit more optimistic (Fig. 7). However, it is obvious that the ratio of ion concentration in the permeate $c_{i,per,model}/c_{i,per,exp}$ is the only important factor for predictive purposes.
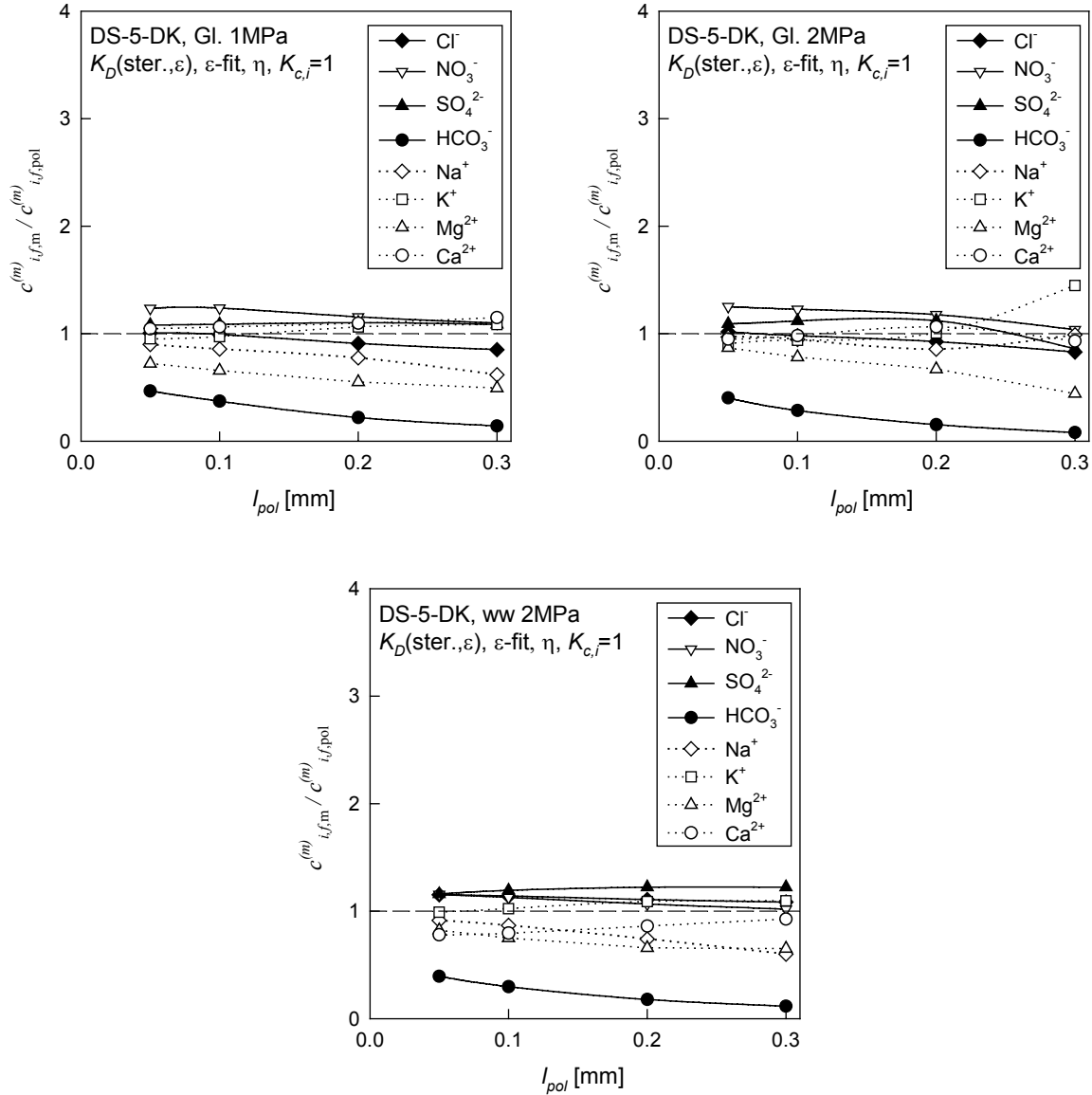

Fig. 7. Ratio of $c^{(m)}_{i,f,m} / c^{(m)}_{i,f,pol}$ vs l_{pol}, model with K_D, η_p given by eqs.(10), (12), respectively; $K_{c,i}=1$; dielectric constant of pore solution is fitted; membrane DS-5-DK, a) Gliwice 1 MPa, b) Gliwice 2 MPa, c) tap water 2 Mpa.

In **Fig. 8** the fitting parameters – X_m, r_p, and ε_p – are presented. It is seen that the density of fixed charges is very low (<3 mol/m^3) and practically always positive. The pore radius is ca. 0.8 for

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variant 1 and 0.6 nm for variant 2. These values of r_p are similar to those obtained by other workers. The dielectric constant of pore solution is about half of that of water which seems to be reasonable.
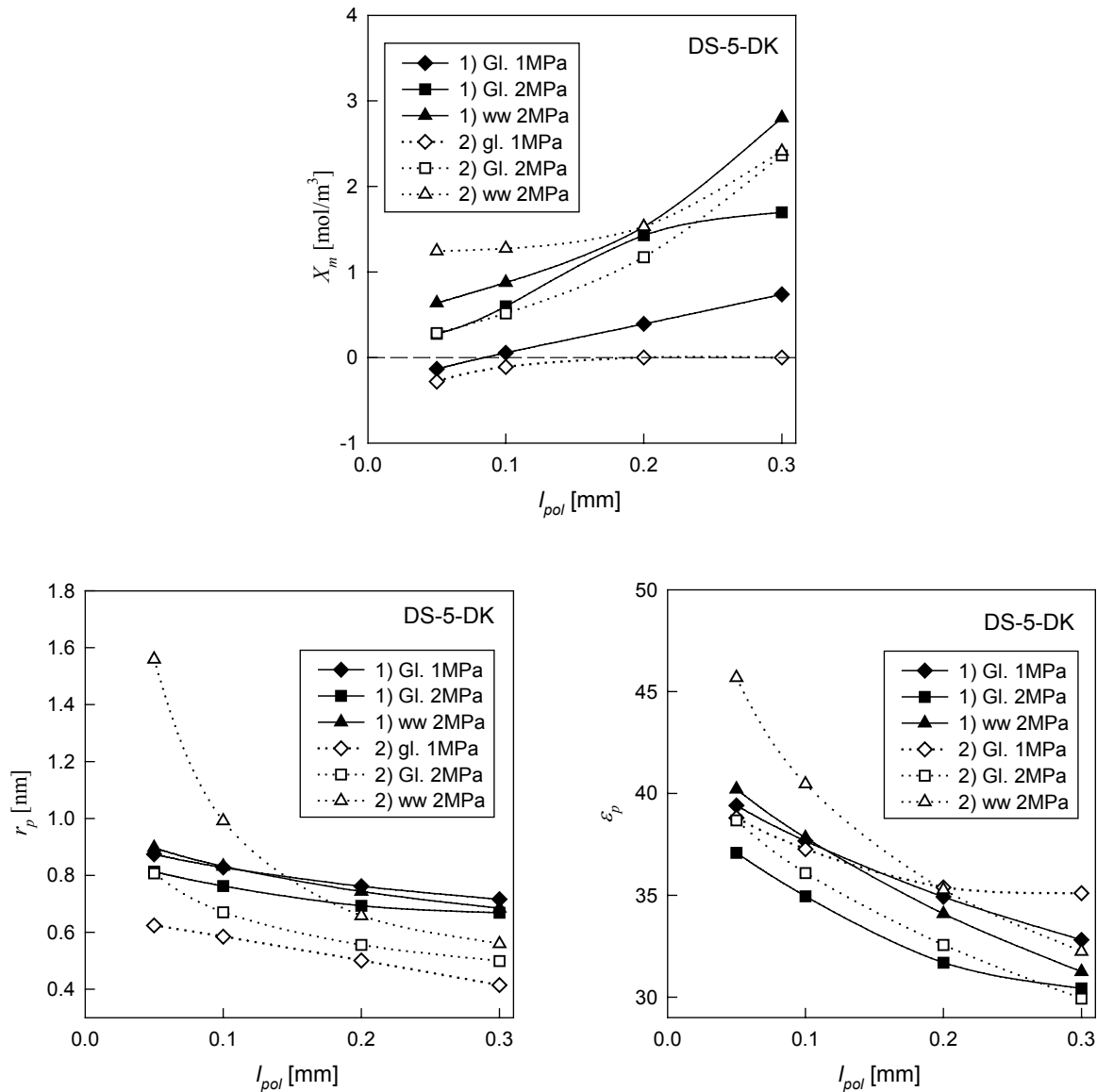

Fig. 8. DS-5-DK, fitting parameters of model variants 1 and 2 for all waters; a) X_m, b) r_p, c) ε_p (for variant 1 ε_p is not fitted but calculated from eq. (18) using fitted r_p).

One would expect that the geometrical parameter – radius of pores – should be the same for ww 2 MPa, Gliwice 1 MPa, and Gliwice 2 MPa (unless the impact of pressure for the same water Gliwice or sorption of an ion on the wall change the flow in the case of tap water - Gliwice). However it is not so, although variant 1 produces pretty good effects; the r_p's calculated from these three NF experiments correlate most.

Since the ratio of length of pores to their area fraction, l_p/X_p (eq.(24)) and the ratio of pore solution to water viscosities, η_p/η_0 (eq.(18)) (Fig. 9) depend on r_p, our observations for those quantities are also similar.

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A comparison of the obtained values of parameters with the ones presented by other authors [ii] who applied different uncharged solutes (Table 2, p 1805) and obtained l_p/X_p from 0.39 to 2.65 µm, r_p=0.61-0.87 nm for membrane CA30 reveals correlations between them.
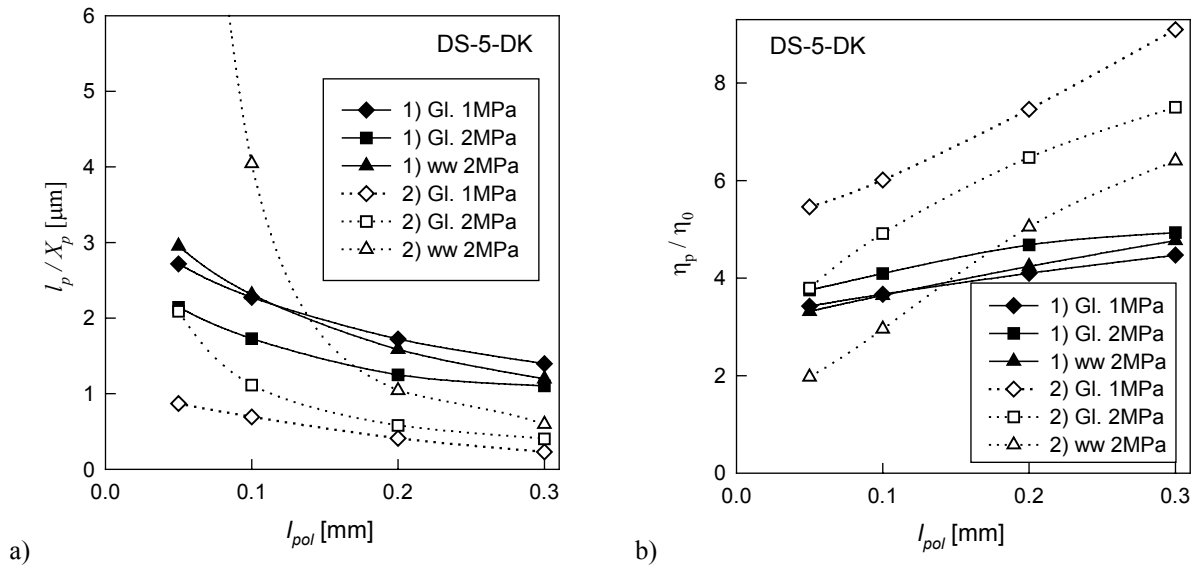

Fig. 9. a) ratio of length of pores to their area fraction, l_p/X_p, calculated from eq.(24) and fitted r_p, b) the ratio of pore and water viscosities, η_p/η_0, calculated from eq.(18) and fitted r_p

Conclusions

The results of nanofiltration of natural waters have been described using the extended Nernst–Planck equation. The model of NF based on that transport equation and on the partition coefficient depending on the Donnan potential and the solvation energy term, taking into account membrane structural parameters and ionic composition of waters, effective for ternary systems, in the case of real multiionc solutions (no. of ions 8) needs further improvement.

It seems that the key to "success" is a suitable description of the partition coefficients of ions. The interactions between ions and the membrane in the transport are of lesser importance.

Acknowledgements

List of symbols

c_i – concentration of species i [mol/m^3],

$\overline{c}_i$ – concentration of species i in the pore solution [mol/m^3],

D_i – bulk diffusion coefficient of ion i [m^2/s],

$\overline{D}_i$ – diffusion coefficient of ion i in the pore solution [m^2/s],

F – Faraday constant, F=96487 C/mol,

J_v – volume flux (based on membrane area) [m/s],

$K_{c,i}$ – hindrance factor for convection [-],

$K_{d,i}$ – hindrance factor for diffusion [-],

l_p – length of pores [m],

l_{pol} – thickness of polarisation layer [m],

N_A – Avogadro number, N_A=6.022·10^{23} 1/mol,

r_i – radius of ion i [m],

r_p – radius of pores [m],

R – gas constant, R=8.314 J/mol·K,

T – absolute temperature [K],

X_m – effective charge density [mol/m^3],

X_p – surface fraction of pores [-],

z_i – valence of ion [-],

ε_0 – permittivity of vacuum, 8.8542·10^{-12} C/V·m,

ε_b – dielectric constant of bulk solution [-],

ε_p – dielectric constant of pore solution [-],

η_p – viscosity of solution [Pa·s],

ψ - electric potential [V],

subscripts: f – feed, p – pore, per – permeate

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