

The Sorption of Metals on the Polysulfone Cation Exchange Membranes

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The sorption of NaCl and CaCl₂ and monovalent-divalent cation salt mixtures on the polysulfone and polysulfone with polyester support cation exchange membranes were investigated. The sorption of monovalent-divalent cation salt mixtures in contact with NaCl+CaCl₂ salt mixtures were studied at a total concentration of 0.05 M. The obtained results for polysulfone type membranes were compared with Neosepta CL-25T and CM2 cation exchange membranes.

Key Words: Sorption, charged membranes, permselectivity, ion-exchange isotherm

Introduction

In the majority of industrial applications which involve ion exchange membranes, and generally, ionic transport is accomplished by the application of an electric field. Membrane transport phenomena are controlled by several factors such as ionic concentration within the membrane, charge density of the membrane, composition of the solution, ionic fluxes and water content. It has been recognized that membrane charge and its density are among the most important factors which characterize membranes. The membrane charge plays an important role in the transport processes¹⁻³ and affects the selectivity of the membrane for charged molecules⁴. The characterization of charged membranes has been studied by many researchers⁵⁻⁹ both theoretically and experimentally.

The behavior of the ions in the membrane phase is very complex and cannot be completely elucidated. The nature of the interaction between the membrane matrix and the ions in relation to the electrochemical behavior of the membranes is also very important. Therefore, this study was undertaken in order to explain the electrical transport phenomena in the new patented ion-exchange membranes. It is known that the ionic transport mechanism is completely different from the transport mechanism in a liquid. The mobility of any particle in the membrane is influenced by interactions with the charged polymer network, friction with water molecules in the electroosmotic flow directed towards the flow of counter-ions and mutual interactions with another transported species¹⁰.

It is of interest to compare the mobility of cations in the polysulfone membranes, because their structure has to be studied extensively to determine whether they are available as a separation material in various electrodialysis and electrosynthetic applications. Much of the research concerning the structure,

ion transport properties and various applications such as solid polymer electrolyte or proton conductors of Nafion membranes has been described in recent monographs^{11–14}. The polysulfone membranes offer controlled ion-exchange capacities and excellent mechanical wet strength and are recommended for post-treatment processes. The other advantage is that the membranes have the necessary chemical stability. Therefore, the electrochemical and ionic transport properties are needed for various applications.

In this paper we report on the sorption of alkali and divalent cations and monovalent/divalent salt mixtures in the polysulfone cation exchange membranes. The combined set of data can be used to gain insights into the structure and behavior of binary cationic mixtures of different valences in the membranes. For this reason, the present study was undertaken to clarify the physicochemical processes which govern the partitioning of monovalent/divalent salt mixtures in polysulfone cation exchange membranes.

Experimental

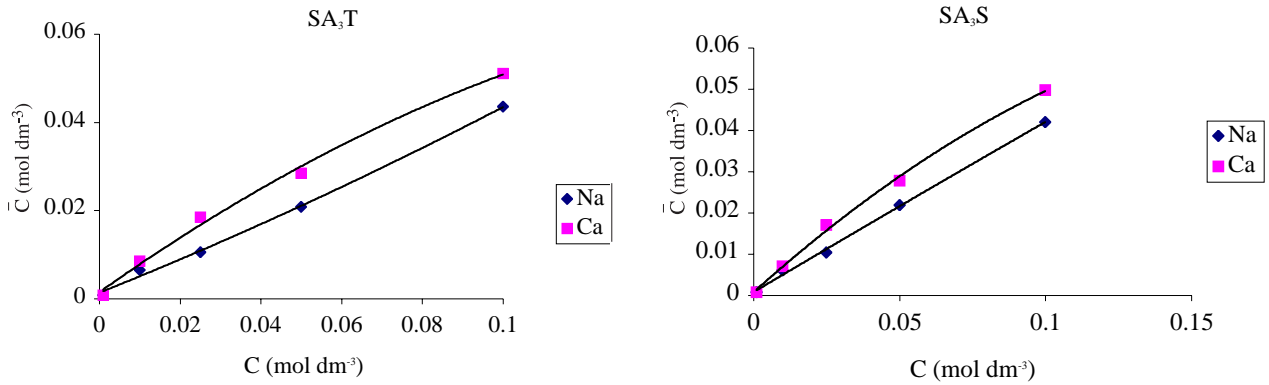
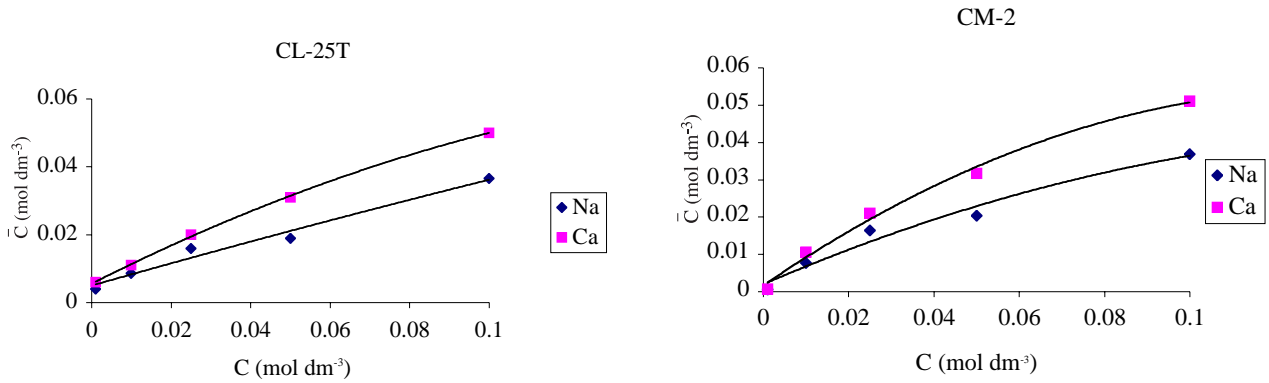
The cation exchange membranes, ICE-450 polysulfone composition (SA₃S, homogeneous), and polysulfone with polyester support (SA₃T, heterogeneous) from Gelman Sciences, were used and Neosepta CL-25T and CM2 cation exchange membranes from Tokuyoma Soda Co. were used for comparisons. Basic specifications of both of the polysulfone membranes are as follows: ion exchange capacity 14 meq. per 47 mm disc, pore size 0.45 μm and thickness 152.4 μm . The cation exchange membranes were supplied in hydrogen form. Chemicals were analytical grade, from Merck, Darmstadt, Germany.

The membrane pieces were first pretreated by boiling for 60 min in deionized water, followed with 1.0 M HNO₃, NaOH and finally distilled water, and then the membrane discs were pretreated with 1.0 M HCl for 24 h to convert the H⁺ form. Sorption experiments were determined by the saturation of the membrane with NaCl or CaCl₂ salts of various concentrations, and then desorption with acid. Membrane samples were soaked in salt solutions of various concentrations for 24 h. No chloride ions were detected in the membranes. They were then blotted quickly with filter paper and soaked in acid for 2 h. The amount of Na⁺ or Ca²⁺ ions desorbed was determined by flame photometry (Corning) and atomic absorption spectrophotometry (Pye Unicam 929). The partition coefficient, K , was calculated using $K = (\bar{C}/C)$.

The equilibrium uptake of monovalent/divalent cations was measured in polysulfone cation exchange membranes from external binary salt solutions mixtures at 25°C. The membranes were equilibrated with aqueous solutions of NaCl-CaCl₂ mixtures with the following equivalent fractions: 1, 0.80, 0.60, 0.50, 0.40, 0.20, and 0 for 24 h. The solution concentration was adjusted at the total concentrations as 0.05 mol dm⁻³. After equilibration, the membrane samples were removed from the salt solutions and the surface of each strip was wiped with filter paper to remove excess electrolyte from the surface. Each membrane sample was then soaked twice in 20 ml of 2.0 M H₂SO₄ to extract mobile monovalent and divalent cations. The accumulated leaching solutions for a membrane sample were collected and analyzed as given above.

Results and Discussion

Sorption of ions is strongly affected by the fixed charge density of the membranes. Figures 1 and 2 show the sorption isotherms of sodium and calcium salts for SA₃T and SA₃S polysulfone, and CL-25T and CM2 membranes, respectively. In this figure, C is the external salt concentration and \bar{C} is the salt concentration in the membrane. The sorption isotherms of the salt were found to be partition type for all the membranes. The partition coefficients were obtained from the slopes of the isotherms and are summarized in the Table.

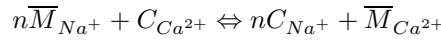

Figure 1. Sorption isotherms of polysulfone membranes for Na^+ and Ca^{2+}

Figure 2. Sorption isotherms of Neosepta membranes for Na^+ and Ca^{2+}
Table 1. Some parameters of the membranes

Membrane	Partition Coefficients		Mmol of charges	Effective charge ratios (\bar{X}/C_s)	
	$K_{(Na^+)}$	$K_{(Ca^{2+})}$		NaCl	CaCl ₂
SA ₃ S	0.432	0.535	0.676	0.211	0.256
SA ₃ T	0.424	0.518	0.687	0.216	0.268
CL-25T	0.384	0.542	0.782	0.378	0.320
CM2	0.392	0.554	0.766	0.306	0.334

The concentration dependence of the partitioning is best described by sorption isotherms¹⁵. These are plots of the molal equilibrium concentrations of solute in the membrane versus the molal concentration in the aqueous solution at a given experimental condition. Straight lines over the whole concentration range would be obtained if the two phases behaved as ideal solutions¹⁶. As seen in Figs. 1 and 2, the ion exchange sites of the polysulfonated membrane are preferentially balanced by Ca^{2+} ions. It has been previously reported that the selectivity of any exchanger could be integrated over all ionic compositions when the ionic fraction is 0.5¹⁷. When the preferences of the polysulfone membranes are compared at an ionic fraction of 0.5, the permselectivity of the membranes for Ca^{2+} ions is higher than that for Na^+ ions.

It is well known that the mobilities of ions within the membrane behave as a function of the external concentrations. Therefore, it was decided to start this work by firstly looking at the equilibrium properties of the membranes with monovalent and divalent salts and then the mixtures of monovalent/divalent salt mixtures to determine the permselectivity of the membranes.

The results of permselectivity measurements in ion exchange investigations are usually illustrated as isotherms: the mole or equivalent fraction of one of the competing ions in the exchanger or membranes is plotted versus those of the same ions in a solution at a given concentration and temperature. The ion exchange isotherm shows the ionic composition of the ion exchange membranes as a function of the experimental conditions. Ion exchange equilibrium is established when an ion exchanger is placed in an electrolyte solution containing counter-ions in which the membrane is in Na^+ form and is equilibrated containing Na^+-Ca^{2+} ions of salt mixture and ionexchange takes place as follows:



where \overline{M}_{Na^+} and $\overline{M}_{Ca^{2+}}$ represent the equivalent fractions of the counter ions in the membrane phase, and $C_{Ca^{2+}}$ and C_{Na^+} , the corresponding equivalent fraction of these ions in the solution phase. In the equilibrium, the membrane and solution contain both ions, and the total amount of exchange sites is equal to exchange capacity¹⁰:

$$N = \overline{n}_{Na^+} + \overline{n}_{Ca^{2+}}$$

where \overline{n}_i , is expressed in mol of charge equivalent. Figs. 3 and 4 show that the above equation is verified taking into account exchanging sites for the studied membranes.

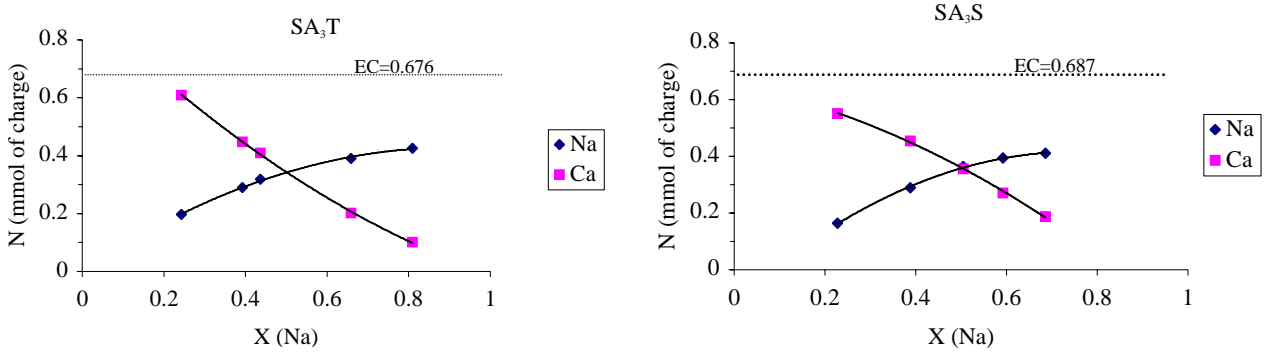


Figure 3. Total exchange for polysulfone membranes equilibrated in $[NaCl]+2[CaCl_2]=0.05$ M. The horizontal line: exchange capacity of the membranes.

The ion exchange isotherms for $Na^+ - Ca^{2+}$ system in both solution and membrane phases can be given as follows:

$$X_{Na^+} = \frac{n_{Na^+}}{n_{Na^+} + n_{Ca^{2+}}}$$

and

$$\overline{X}_{Na^+} = \frac{\overline{n}_{Na^+}}{\overline{n}_{Na^+} + \overline{n}_{Ca^{2+}}}$$

In order to clarify the permselectivity of the polysulfonated membranes towards monovalent/divalent cations, the NaCl-CaCl₂ system was chosen. Figures 5 and 6 show the equilibrium cation concentration in polysulfone and Neosepta cation exchange membranes at 25°C and at a total external salt concentration of 0.05 M. It can be seen that the membranes show preferential sorption for Ca²⁺ ions when the external concentration for both cations is equal.

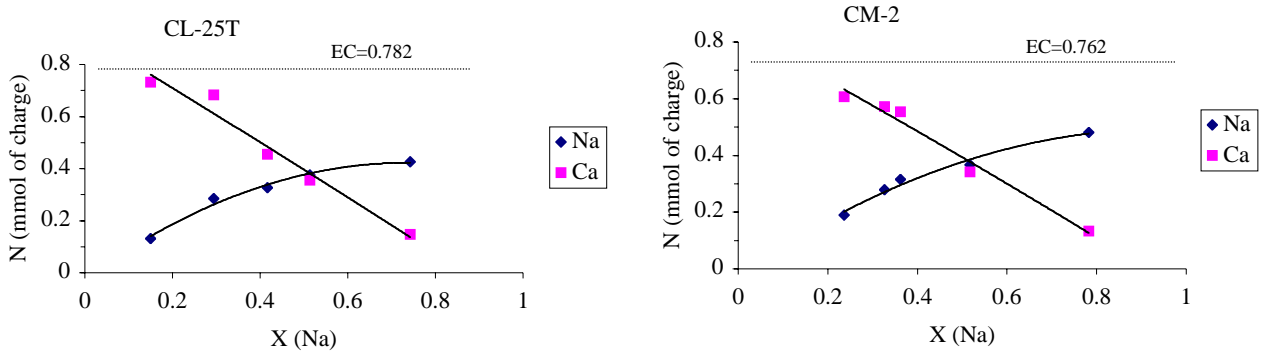


Figure 4. Total exchange for Neosepta membranes equilibrated in $[NaCl]+2[CaCl_2] = 0.05$ M. The horizontal line: exchange capacity of the membranes.

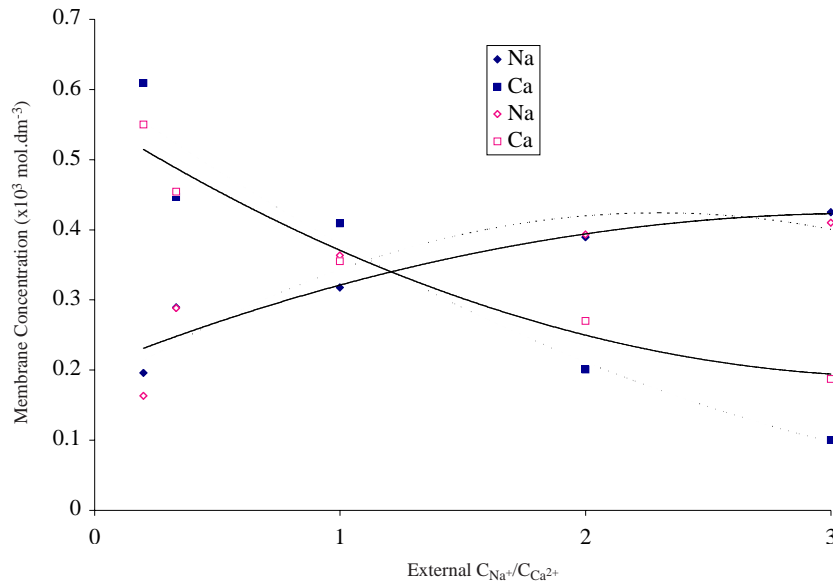


Figure 5. Equilibrium cation concentration in polysulfone membranes at total concentration 0.05 M. Light symbols and dotted lines for SA₃S and bold symbols and dashed lines for SA₃T membranes.

The attracting interaction between the metal ions and the water molecules is primarily electrostatic in character. Ionic solvation phenomena play a role in ion exchange selectivity theories in which selectivity is governed by the free energies of hydration, which is independent of the size and charge of ion species and of the solvent type. The calculated hydration constant values for Ca²⁺ and Na⁺ ions are 8.10×10^5 and 2.09×10^5 J mol⁻¹, respectively^{18,19}. The overall permselectivity of the ion-exchange membrane is governed by the equilibrium solubility of ions at the membrane/solution interfaces and ion diffusivity through the

interior region of the membrane. Bontha and Pintaura¹⁹ developed the equilibrium partitioning model for monovalent/divalent cation permselectivity in membranes and they reported that the cation selectivity sequence, where the cation exclusion from the membrane was preferentially influenced by higher surface charge density, and the following effects were assumed: (i) ion/fixed-charge site electrostatic interactions in the cylindrical pores of the membrane, (ii) solvent dipole alignment by the radial direction electric field generated by the membranes fixed-charge sites, and (iii) ion hydration free energy changes which occur when ions solubilize in the low-dielectric constant pore fluid¹⁹.

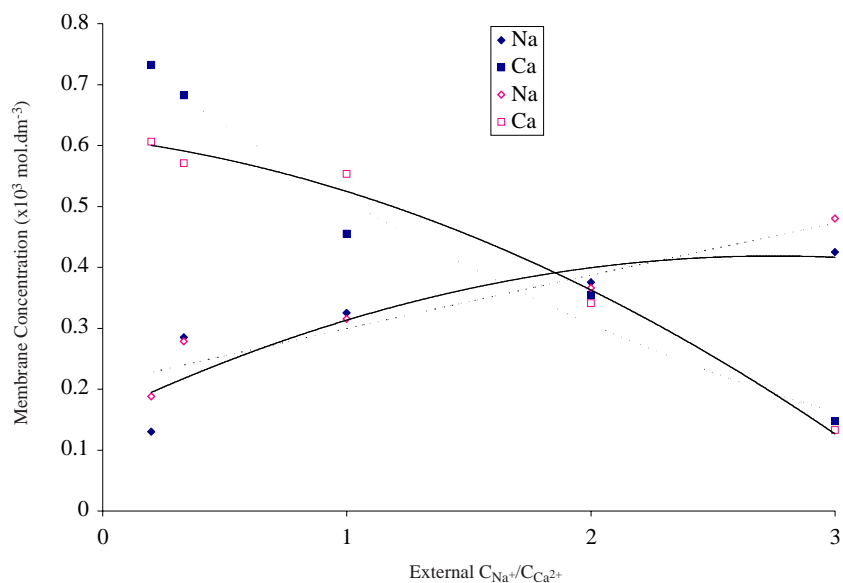


Figure 6. Equilibrium cation concentration in Neosepta membranes at total concentration 0.05 M. Light symbols and dotted lines for CM2 and bold symbols and dashed lines for CL-25T membranes.

The transport properties of phosphonic acid and sulfonic acid cation exchange membranes were studied and their transport permselectivity for monovalent/divalent cations was compared²⁰. It was founded that the permselectivity of Ca^{2+} over Na^+ ions for the phosphonic acid membrane was lower than that of the sulfonic acid cation exchange membrane. The relative transport number and ion exchange equilibrium constant of Ca^{2+} over Na^+ ions for phosphonic acid and sulfonic acid cation exchange membranes were found to be 2 and 4, respectively²⁰.

The selectivity order in a Nafion perfluorosulfuric acid cation-exchange membrane was found to be $Cs^+ > Rb^+ > Ba^{+2} > K^+ > Mg^{2+} > Na^+ > H^+ > Li^+$ for a mixture of univalent/divalent cation systems²¹. A similar sequence was also observed for Neosepta, Selemion, Aciplex and Nafion membranes^{22,23}. The selectivity of a binary solution such as Ca^{2+} or Cu^{2+} with Na^+ or protons in cation exchange membranes was studied and the selective uptake of divalent cation species over monovalent species was observed²⁴. It was reported selective phenomena depend on the higher electrostatic attraction between divalent cations and the fixed charge sites within the membrane. This suggests that the hydration radii play a role in the permselectivity of ion exchange membranes and that the permselectivity of any ion can be governed by ion partitioning at the membrane/solution interface.

Multicomponent equilibrium partition coefficient model on a molecular-level basis was formulated by Bontha and Pintaura²⁵ who reported that the ion with the lower surface charge density (i.e., the monovalent

ion with the largest hard sphere radius) was preferentially adsorbed into Nafion cation exchange membranes. The divalent/monovalent cation concentration ratio in the membrane was determined and found to be greater than one. The absorptions of Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and Pb^{2+} were compared with monovalent cations in Dowex 50 poly(styrene-sulfonic acid) cation exchange resins, in which the absorption of divalent cations was found to be higher than that of monovalent cations²⁶. The equilibrium partitioning of Zn^{2+} and Na^+ aqueous solutions in Dowex 50 was investigated and the selective uptake of Zn^{2+} was higher than that of Na^+ ²⁷. The absorption of singly and multiply-charged metal ions in cation-exchange gels of various cross-linking was examined by many investigators and it was found that large decreases in volume and positive entropy changes occurred when heavily cross-linked gels were exposed to multivalent cations²⁸. We can conclude that such cations release a portion of their water of coordination and form contact ion pairs with the polymer matrixs charged sites. There is another possible explanation for the same study: field binding (solvent-separated ion pairs) of monovalent cations was inferred from enthalpy and entropy measurements with lightly cross-linked gels. Divalent cation/hydrogen ion uptake in Nafion membranes was studied^{21,29} and the larger cation is selectively absorbed¹⁰.

The equilibrium uptake of monovalent/divalent cations on polysulfone and polysulfone supported with polyester cation exchange membranes was investigated experimentally as a function of mole fraction. Experimental membrane cation concentrations were correlated with sorption isotherms. For the sorption of cations, ion hydration effects, the dielectric saturation of water molecules in the membrane matrix due to the electric field generated by the fixed-charge sites, and the neutralization of some fixed-charges by ion pairing between divalent cations and sulfonate ion exchange sites were considered.

The mechanism of specific permselectivity of a cation exchange membrane is due to the different electrostatic repulsion forces of ions relative to the cationic charge on the membrane surface. It has been previously reported that a cation exchange membrane is preferentially permeable to cations lower rather than higher valency and to larger hydrated cations rather than smaller³⁰⁻³³. Sata and Izuo³¹ studied the permselectivity of Ca^{2+} ions to Na^+ ions using Neosepta CL-25T membrane and found that the permselectivity of Ca^{2+} ions is higher than that of Na^+ ions.

Conclusion

It is considered that the ions in the membranes are hydrated in a manner similar to that in aqueous solution. In other words, the ionic mobility ratio in the membrane is more strongly influenced by the cation of smaller radius. It can be pointed out that the interaction between cations and the fixed anionic charge is reduced by hydration of the ions. From the results, it can be concluded that the extent of monovalent cation uptake, in combination with the need to maintain electroneutrality in the membrane bulk polymer network, regulates the absorption of mobile divalent cations. This result is not entirely expected since the low surface charge density monovalent cations are affected by repulsive hydration forces. Thus, a membrane polymer network with a high concentration of M^+ requires fewer mobile M^{2+} ions to establish charge-balance mobile anions and sulfonate fixed-charges.

Acknowledgement

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List of Symbols

C_i	concentration of ion i in solution phase (mmol/cm ³)
\overline{C}_i	concentration of ion i in the membrane phase (mmol/cm ³).
C_s	concentration of fixed sites (equiv./cm ³)
K	partition coefficient
\overline{M}_i	equivalent fractions of ion i in the membrane phase
n_i	number of ionic equivalents in solution phase
\overline{n}_i	number of ionic equivalents in membrane phase
N	individual ionic concentration in membrane (mmol/cm ³)
X_i	equivalent fractions of ion i in solution phase
\overline{X}_i	equivalent fractions of ion i in membrane phase

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