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Influence of Amphoteric Behaviour of Oxide Materials on the Selectivity of Micro and Mesoporous Ceramic Membranes

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Electrostatic interaction is a very important parameter for the membrane selectivity. In this work, the electrical double layer establisment on the surface of metal oxide material from the Stern-Grahame model has been described. Then, some examples of rejection using micro and mesoporous ceramic membranes have been given. A correlation between the charges of the membrane material and the species to be filtered has been precised. Two rejection mechanisms have to be taken into account the size of the solutes and the electrostatic interactions.

Introduction

Nanofiltration (NF) can be defined by the pore diameter size, in the range 0.5 to 2 nm or by the membrane cut-off from 300 to 1 000 D. The interest of nanofiltration is due to the salt rejection particularly for multivalent ions, to the higher permeability and lower working pressure than those of reverse osmosis. The lowest range of UF (pore diameters less than about 10 nm) can be associated to NF for the mechanisms of ion rejection.

In case of neutral species, the criteriom of solute size related to pore diameters is preponderant. For ionic species as salts, the rejection cannot be explained by the size exclusion. Electrostatic interaction has to be considered. The model of Levine *et al.*[1] can be used to predict the rejection rate. Ion rejection increases when membrane charge and co-ion charge increase too and ion rejection decreases when ionic strength increases. it is clear that electric interactions are dominant for the selectivity of the membranes.

In the literature, it can be found many examples on the influence of membrane charge on the performances of organic membranes.[2,3] These studies have been also applied for instance to avoid the fouling of organic membranes by proteins[4]; electrostatic repulsion acts to decrease adsorption and flux reduction.

If we are looking at the earliest definition of nanofiltration, which was also named hyperfiltration, only was mentionned the anion rejection due to a negative residual charge of organic membranes.[5] This model is now applied to inorganic ones[6] to explain the rejection of anions and cations due to the amphoteric behaviour of the oxide material by using the triple layer model.[7]

Electrical double layer

In case of ceramic membranes, the oxide material has am-

photeric properties and it can be positively or negatively charged depending of the pH value:

$$M\text{-}OH + H^+ \Leftrightarrow M\text{-}OH_2^+$$
$$M\text{-}OH + OH^- \Leftrightarrow M\text{-}O^- + H_2O$$
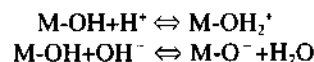
In an electrolyte solution the total charge of ceramic particles is also due to the redistribution of the counter-ions according to the complexation reactions:

$$M\text{-}OH_2^+ + A^- - M\text{-}OH_2^+ \dots A^-$$
$$M\text{-}O^- + C^+ - M\text{-}O^- \dots C^+$$
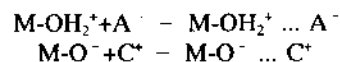
The distribution of the ions in the solution is modified: the co-ions are rejected and the counter-ions are attracted by the membrane surface. Different models were developed for explaining these phenomena and answer to the question: what is the origin of the electrical double layer? The Stern-Grahame model can be used and described as follows: a particle, immersed in a solution, acquires a surface charge and accumulates a counter-charge in order to preserve global electroneutrality; this counter-charge layer or compact layer is surrounded by a diffuse layer. Surface, compact, and diffuse layer charges make up the electrical double layer (Figure 1).

Amphoteric reactions take place on the O plane. Complexation reactions occur on the β plane. The d plane is the limit between compact and diffuse layers. The compact layer is moving with particles when they are put in an electric field.

The potential decreases linearly between charge planes in the compact layer and presents an analogy with parallel plate capacitors in series. The potential on the d plane φ_d is called zeta-potential (ζ potential). In the diffuse layer, excess number of counter-ions decreases exponentially until the concentrations of positive and negative ions are equal like in the bulk solution. The potential varies according to the reduced Poisson-Boltzmann equation:
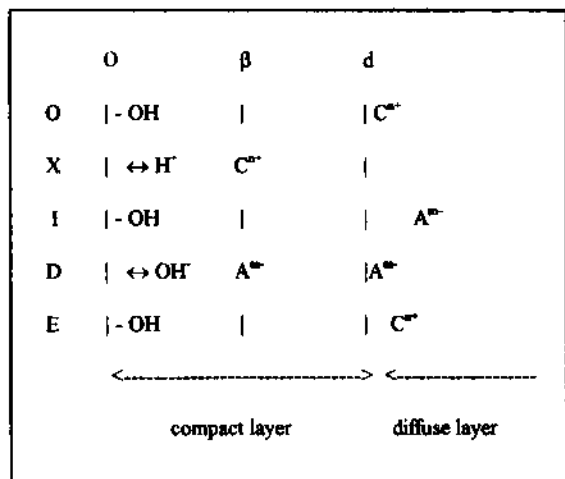
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Figure 1. Stern-Grahame model or electrical double layer.

$$\varphi = \varphi_d \exp\left(- \kappa\, x\right)$$

where x is the distance between the diffuse layer and the d plane, and $\kappa = 2\,(e^2/\varepsilon kT)\,I$ where e=electron charge, ε=dielectric constant, k=Boltzmann constant, T=temperature and I= ionic strength.

The diffuse layer thickness is measured by the Debye length parameter: κ^{-1}.

Surface charge can be measured by titration using acid and base solutions. From this value, the Point of Zero Charge (PZC) will be determined. The pH of the PZC is the pH value at which the surface charge density σ_0 is zero.

Double electric layer can be characterized by determining the zeta potential value from electrophoretic mobility measurements. The pH of the Iso-Electric Point (IEP) is the pH value at which the number of negative and positive charges are equal (σ_d=0); at this point, the mobility is zero.

Surface charge density σ_0 is investigated for powder suspension in electrolyte solution. Titration is followed by potentiometric measurements using acid and base solutions.

$$q(H^+)_a = q(H^+)_t - q(H^+)_s$$

with $q(H^+)$ is the quantity of protons and a, t and s denote respectively the quantity adsorbed, the total quantity added in the solution and the quantity free in the solution after equilibrium.

The surface charge density is calculated with the following equation:

$$\sigma_0 = q(H^+)_a \cdot 96\ 500/m \cdot S \quad (C/cm^2)$$

with m=mass of powder and S=specific surface area.

The variation of σ_0 intercepts the pH axis at the value of ZPC.

The ZPC value can be also determined by the variation of the pH of an electrolyte solution after adding powder. The curves of final pH versus initial pH give the ZPC value at the inflection point.

For electrophoresis, the mobility (μ) of the charged particles under the influence of an electric field is measured as a function of the velocity V and the value of the electric field E:

$$\mu = V/E \quad (m^2 \cdot V^{-1} s^{-1})$$

The mobility is directly linked to the potential of the shear plane which corresponds to the ζ potential by the Smoluchowski equation: $\mu = \varepsilon \cdot \zeta/\eta$ if $a/\kappa^{-1} > 100$ or Hückel equation: $\mu = 2\varepsilon \cdot \zeta/3\eta$ if $a/\kappa^{-1} < 1$ with η=the viscosity, a=particle radius and κ^{-1}=Debye length.

In practice, only the value of the particle speed and the sign of the material charge are important for explaining the repulsion Donnan effect and the selectivity of the membranes.

Experimental and Results

Surface charge and Point of Zero Charge. Characterization of the membrane material was performed using the powder, which was the same one for preparing the membrane.

The surface charges were measured by acid-base titrations. The pH value of the PZC was determined from the variation of the surface charge as a function of pH or from the variation of the pH of the solution in which powder was immersed.

The IEP was determined from the variation of the mobility or of the ζ-potential of the particles immersed in a constant ionic strength solution versus pH and nature of electrolyte.

The selectivity of the potassium titanyl phosphate (KTiOPO$_4$) membranes[8] was determined by measuring the ion rejection using an ionic chromatography. A laboratory pilot was used for the filtration tests.

We have used three different membranes according to their pore diameters. They were fired at 400, 500 and 550 °C respectively noted M400, M500 and M550 with pore diameters equal to 2.4 nm, 5 nm and 10 nm. The first ones are in the range of micropores and the other ones are in the range of mesopores.

PZC determination: In Figure 2, the results of the titration of a suspension of KTP powder fired at 550 °C are reported. The surface charge density-pH curves are given in Figure 3.

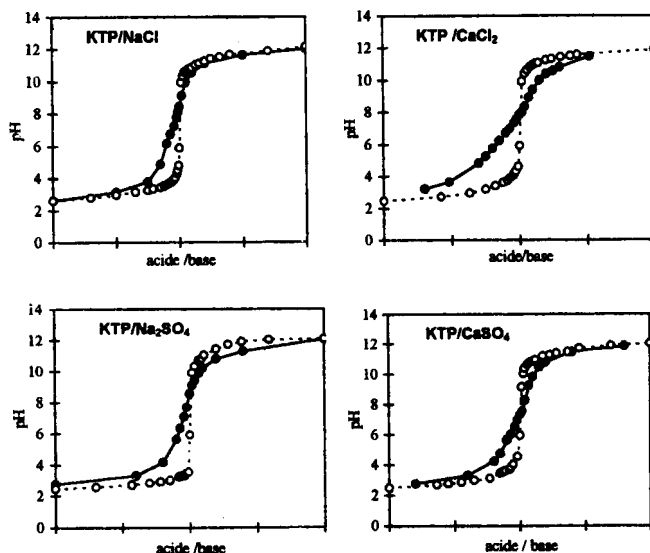KTiOPO$_4$ powder was added in an electrolyte solution at

Figure 2. Titration curves in various electrolyte solutions (○ : electrolyte solution, ● : electrolyte solution+suspended powder).
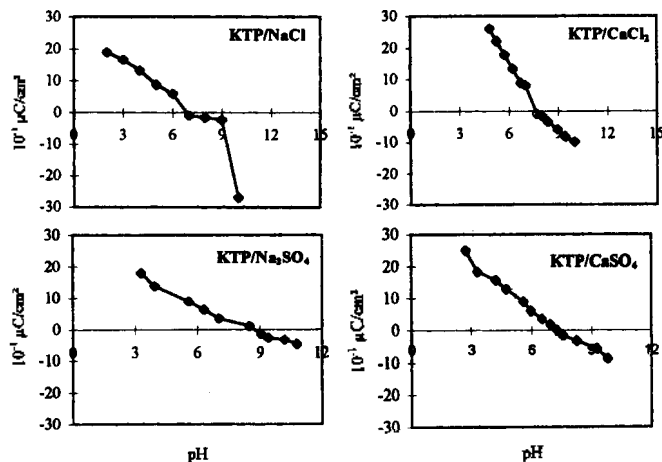
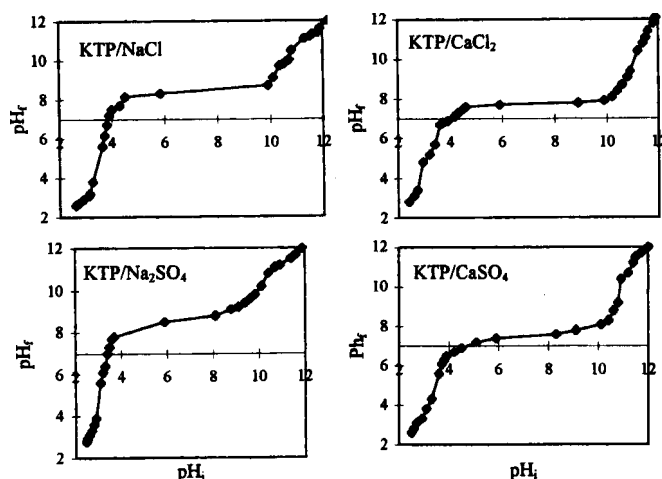**Figure 3.** Value of surface charge density versus pH.

Figure 4. Variation of final pH as a function of initial one.

pH$_i$; after equilibrium pH stabilizes at pH$_f$. The variation of pH is reported in Figure 4. The PZC value was determined at the inflection point.

In alkaline part a more important displacement is observed with Ca^{2+} than with Na$^+$. A more marked effect is noted in acid part than in alkaline part.

In Table 1, the PZC value determined by the two methods are compared. A good agreement is noted.

Global charge and Iso Electric Point. The global charge of the particles was characterized by electrophoresis by measuring their mobility in an electric field. For this study, four types of electrolytes were choosen: NaCl, CaCl$_2$, Na$_2$SO$_4$ and CaSO$_4$. The electrolyte concentration was equal to 10^{-3} M.

In all cases, the charge of the membranes is negative in all over the pH range as it can be observed in Figure 5 us-

Table 1. Comparison of the PZC values determined from titration curves (PZC 1) and from pH variation (PZC 2)

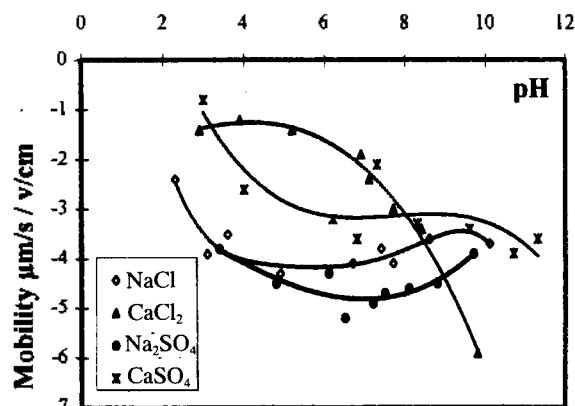|	NaCl	CaCl$_2$	Na$_2$SO$_4$	CaSO$_4$
PZC 1	7.2	7.5	8.5	7.2
PZC 2	8.1	7.7	8.5	7.3

Figure 5. Mobility of KTiOPO$_4$ powder.

Table 2. Rejection of salt solutions from different pore diameters

	NaCl	Na$_2$SO$_4$	CaCl$_2$	CaSO$_4$
M400	51	87	16	52
M500	48	64	16	46
M550	44	46	14	37

ing M550 membrane.

We can note that: (i) in case of Na$_2$SO$_4$ (1 : 2 electrolyte) the negative charge is the highest; (ii) in case of CaCl$_2$ (2 : 1 electrolyte) the negative charge is the lowest in the pH range 2 to 8; (iii) for (1 : 1) and (2 : 2) electrolytes, the negative charge is intermediate between (1 : 2) and (2 : 1) electrolytes. The value of IEP can not be determined with this material.

Results of rejection. The filtration of salt solutions was performed using the same preceding solutions at the same concentration at 5 bar working pressure. The results of the selectivity of the membranes are reported in Table 2.

It can be observed that the rejection is, of course, better for M400 than the two other membranes. This can be related to the pore size. The rejection is high in case of divalent anion associated with a monovalent cation (like Na$_2$SO$_4$) and low in case of a divalent cation associated with a monovalent anion (CaCl$_2$). Between these two cases, there is a competition between electrostatic repulsion and attraction.

If we are looking at the evolution of rejection rate of the same electolyte as a function of the firing temperature of the membranes, we can remark that the rejection is decreasing from M400 to M550 in case of (2 : 1) and (1 : 2) electrolytes and almost stable if (1 : 1) and (2 : 2) electrolytes are used.

Other experiments were also conducted with charged molecules and neutral ones. Results obtained with M550 are given in Table 3.

Table 3. Rejection of molecules versus molecular weight and charge (TPTZ=tripyridyl-triazine; PEG=poly-ethylene-glycol)

Compound (MW)	Sucrose (342)	Acid orange	Fe(TPTZ)$_3^{2+}$ (992)	PEG (1500)	PEG (4000)
Rejection rate	15	97	12	37	68

With neutral molecules (sucrose and PEG) the rejection rate increases with the molecular weight. The rejection is very low if the membrane has opposite charge than this of charged molecule ($Fe(TPTZ)_3^{2+}$). But whatever the molecular weight, the rejection rate is very high if the molecule has the same charge than this of the membrane (orange acid is negatively charged in aqueous medium). It is clear that the electrostatic interaction (repulsion or attraction) is preponderant for the membrane selectivity.

Discussion and Conclusion

General rules can be given to explain the selectivity of micro- and mesoporous membranes:

*if the molecular weight of the filtered species is higher than the membrane cut-off, the rejection rate will be high;

*if the molecular weight of the filtered species is lower than the membrane cut-off, two cases occur:

- membrane material and species have the same charge, the rejection rate will be high due to the electrostatic repulsion;

- membrane material and species have opposite charges, the rejection rate will be low due the electrostatic attraction.

In all cases, divalent ions have a more important influence than monovalent ones. If monovalent or divalent ions are associated together, there is competition between attraction and repulsion.

The importance of presence of charges on the membrane surface has been pointed out. The transfer phenomenon of ionic species through a membrane depends on the size and on the charge of species in solution. It is based on the Donnan rejection or attraction model. So, the choice of the membrane to be used is very important for its performances. This choice must depend on (i) the nature of ions in solution and their concentration, and (ii) the pH value of the solution which is determining for the charges on the membrane surface.

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