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Feasibility study of selectivity forecast of nanofiltration membranes

A. Kavitskaya*, A. Kononova, D. Kucheruk

*Institute of Colloid and Water Chemistry, Ukrainian National Academy of Sciences,
42 Vernadsky pr., Kiev-142, 03680 Ukraine
Tel. + 38 (044) 424-3575; Fax +38 (044) 423-8224; email: honch@icwc.kiev.ua*

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Abstract

Transport characteristics of nanofiltration membranes OPMN-K, OPMN-KM₃, OPMN-P, and OPMN-KN (produced by “Polimersintez”, Russia) were studied in the process of separation of low concentration solutions of salts NaCl, Na₂SO₄, CaCl₂. Operation areas of the membranes were determined for each salt solution, where the selectivity–volume flow relationship reached its saturation. The data were obtained showing a predominant role of the charge, which determines selectivity of membranes under conditions of separation. We have analyzed a relationship between experimental results and data on the composition of polymers that are used in synthesizing the membranes studied. On the basis of the experimental results an attempt was made to predict the selectivity of membranes in separation of low concentration solutions of salts.

Keywords: Nanofiltration membranes; Ionogenic groups; Charge of membranes; Selectivity

1. Introduction

Nanofiltration (NF) membranes that have recently found wide application in water purification are referred to charged membranes. The nature of

charge of membranes may be different; however, the most intrinsic cases imply the emergence of a charge as a result of dissociation of ionogenic groups that are bound by forces of chemical interaction with a polymer matrix of the membrane. Depending on the chemical nature of an ionogenic

*Corresponding author.

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group a positive or negative fixed charge emerges as a result of dissociation. Ionogenic polymers used for obtaining NF membranes generally contain carboxyl, sulfo or quaternary ammonium groups. The presence of these groups provides for existence of a fixed charge. The charge value of membranes is determined by concentration of ionogenic groups referred either to a unit mass of a dry membrane or to a volume of solution in pores. That is why the selective properties of NF membranes are determined primarily by some or other ionogenic groups present in these membranes [1].

Since the presence of charges on the surface of pores or in the volume of a membrane and consequently the presence of a double electric layer on the interphase or microsections is intrinsic to NF membranes, their retention properties in the region of small concentrations of electrolytes are determined, primarily, by the electrochemical mechanism of ionic separation [2]. As these membranes are highly productive, the maximum possible selectivity can be achieved only under the condition of eliminating the impact of concentration polarization (CP). In this case, the transport characteristics of membranes are characterized by the fact that selectivity (R) does not depend on volume flow (J), i.e., the plot of the R vs. J relationship enters the region of saturation [3]. Selectivity of membranes in the given region for solutions of electrolytes such as 1:1, 1:2, and 2:1 is determined by the primary role of either positive or negative charge of membranes. This, in its turn, indicates chemical nature of the ionogenic group in the composition of polymers used to produce NF membranes.

The purpose of this study was to investigate the transport characteristics of NF membranes in separation of low concentration solutions of salts for finding out the possibilities of making prognosis of selectivity on the basis of the composition of polymers used to produce NF membranes.

2. Experimental

2.1. Membranes

In our investigations we used NF membranes of the following grades: OPMN-K, OPMN-KM₃, OPMN-P, and OPMN-KN (produced by Polimersintez, Russia). In accordance with data from [3] membranes OPMN-K are produced on the basis of polyvinyl alcohol (PVA) and piperazine, cross-kinked with trimezoilchloride; selective layer of OPMN-KM₃ is formed by copolymerization of piperazine and trimezoilchloride in the presence of PVA and benzoic acid [4]; membrane OPMN-P is produced on the basis of piperazine. We have not discovered any information about the composition of polymers used to produce membranes OPMN-KN.

2.2. Solutions

Experiments were conducted on solutions of salts NaCl, Na₂SO₄, and CaCl₂, where concentration of NaCl in the solution was 1.37 g/l, Na₂SO₄ — 1.69 g/l, and CaCl₂ — 2.08 g/l. We used salts of “chempure” grade. Solutions were prepared by dissolving an appropriate weight of salt in distilled water. The pH value of the solutions was 6.5–7 and their temperature was 23±1C.

2.3. Conditions

The experiments were conducted on a circulation plant, the description and basic principles of which were presented in paper [5]. Tangential speed of the solution above the membrane surface was 2.3 m/s. We tested the volume flow and ion concentration of sodium and potassium in filtrates and in the circulating solution every 30 min. The ion concentration was determined by the method of emission flame photometry. Characteristics of the membranes were investigated at working pressures of 0.3, 0.6, 0.9, 1.2, 1.5 MPa. This enabled us to study the impact of the volume flow on selectivity of the membranes. In the experiments at each new pressure value we accepted

for analysis only those indicators (selectivity and volume flow) that remained unchanged during a lengthy period of time (1.5–3 h), i.e. after completion of relaxation processes of rearrangement of the structure of polymer layers [6].

3. Results and discussion

Figs. 1–4 present the relationships of selectivity as a function of volume flow for membranes OPMN-P (Fig. 1), OPMN-K (Fig. 2), OPMN-KM₃ (Fig. 3), and OPMN-KN (Fig. 4) during separation of the solutions of salts NaCl, Na₂SO₄, and CaCl₂.

As can be seen from Fig. 1 for membrane OPMN-P, the curves of the selectivity vs. volume flow relationship reach saturation at one and the same volume flow for all three salt solutions. In this case, the selectivity for sodium and potassium ions reaches 0.90 and 0.85 respectively on solutions Na₂SO₄ and CaCl₂. On the one hand, a high selectivity for the electrolyte solution of type 2:1 (CaCl₂) $R = 0.85$ indicates a predominant role of a positive charge. On the other hand, the value $R = 0.90$ on the electrolyte solution of type 1:2 (Na₂SO₄) reveals the presence of a negative charge since such a high selectivity cannot be determined only by a steric fact (big dimensions of sulfates).

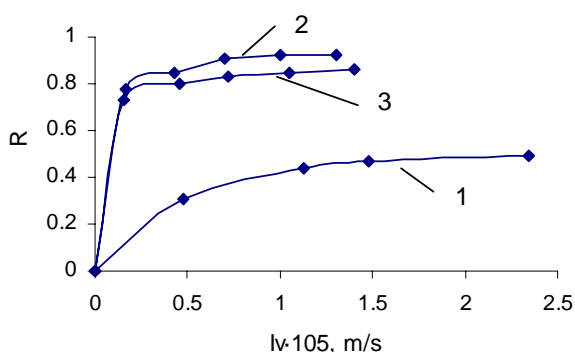


Fig. 1. Relationship of selectivity of membrane OPMN-P as a function of volume flow in the process of separation of solutions: 1 – NaCl, 2 – Na₂SO₄, 3 – CaCl₂. The value of pH = 6.5–7.0, $t = 23 \pm 1^\circ\text{C}$, $v = 2.3$ m/s.

On the basis of data in [7] we can assume that under conditions of separation of solution NaSO₄ a negative charge appears due to a predominant adsorption of double-charged SO₄²⁻ ion by a membrane OPMN-P. Since the value of a charge rather than its sign is important for electrolytes of type 1:1, in the case of NaCl solution, the selectivity value of 0.4 for sodium ions characterizes the membrane as weakly charged. Therefore, the selective properties of membrane OPMN-P are determined, evidently, by ionogenic groups imparting to the membrane primarily a positive charge under conditions of separation.

The investigation of transport characteristics of membrane OPMN-K (Fig. 2) revealed that the trend of the selectivity variation on the solutions of electrolytes of various types was the same as for membrane OPMN-P. This makes it possible to assume that these membranes are similar in terms of their selective properties. However, the selectivity of membrane OPMN-K in the process of separation of electrolytes under study is lower (0.20, 0.63, and 0.73 for NaCl, Na₂SO₄, and CaCl₂ respectively) than that for membrane OPMN-P. One may assume that the selective properties of membrane OPMN-K produced on the basis of PVA and piperazine that were cross-linked with trimezoilchloride are determined by a

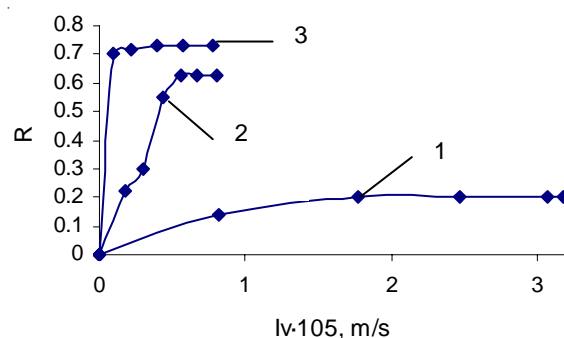


Fig. 2. Relationship of selectivity of membrane OPMN-K as a function of volume flow in the process of separation of solutions: 1 – NaCl, 2 – Na₂SO₄, 3 – CaCl₂. The value of pH = 6.5–7.0, $t = 23 \pm 1^\circ\text{C}$, $v = 2.3$ m/s.

predominant action of amino groups present in piperazine.

Selectivity of membrane OPMN-KM₃ (Fig. 3) is fundamentally different from that of the above membranes. A high value of R in solution Na₂SO₄ (0.90) and low (0.30) in solution CaCl₂ shows the predominant role of a negative charge. A relatively low selectivity $R = 0.40$ in the electrolyte solution of type 1:1 (NaCl) can be related to a small charge of membrane OPMN-KM₃. Hence, it follows that under conditions of separation of solutions the selective properties of membrane OPMN-KM₃ (which is produced by copolymerization of piperazine and trimezoilchloride in the presence of benzoic acid) are determined by the presence of negative ionogenic groups. Such groups may be carboxyl ones since benzoic acid was used in manufacturing of the membrane.

Fig. 4 displays the relationship of selectivity of membrane OPMN-KN as a function of volume flow in separation of solutions of Na₂SO₄ and CaCl₂. As can be seen from Fig. 4, the selectivity of membrane OPMN-KN for calcium ions is comparable with the selectivity for the given ions of membranes OPMN-P (Fig. 1) and OPMN-K (Fig. 2). A gradual increase of the selectivity of membrane OPMN-KN observed in conditions of separation of solution Na₂SO₄ is probably related to adsorption of SO₄²⁻ ions as we earlier suggested in respect to OPMN-P. Since membrane OPMN-KN is similar to membrane OPMN-K in terms of the nature of the selectivity variation and values $R = 0.78$ (CaCl₂) and $R = 0.80$ (Na₂SO₄), it may be considered as positively charged.

4. Conclusions

1. The results of investigations of transport characteristics of NF membranes in the process of separation of low concentration solutions of salts NaCl, Na₂SO₄, and CaCl₂ at pH 6.5–7.0 and under conditions eliminating the effect of CP make it possible to assume that in the case of application

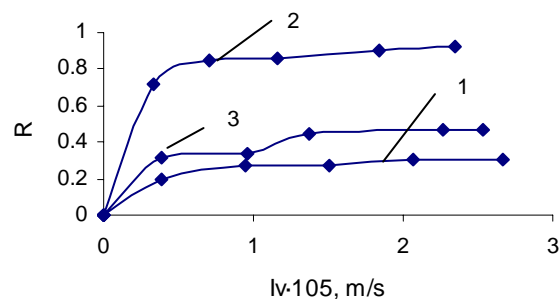


Fig. 3. Relationship of selectivity of membrane OPMN-KM₃ as a function of volume flow in the process of separation of solutions: 1 – NaCl, 2 – Na₂SO₄, 3 – CaCl₂. The value of pH = 6.5–7.0, $t = 23 \pm 1^\circ\text{C}$, $v = 2.3$ m/s.

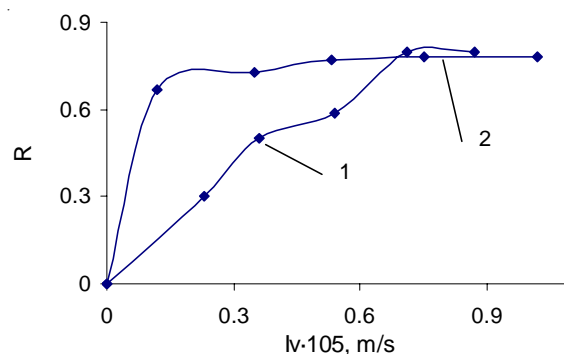


Fig. 4. Relationship of selectivity of membrane OPMN-KN as a function of volume flow in the process of separation of solutions: 1 – Na₂SO₄, 2 – CaCl₂. The value of pH = 6.5–7.0, $t = 23 \pm 1^\circ\text{C}$, $v = 2.3$ m/s.

of membranes produced on the basis of PVA and piperazine cross-linked with trimezoilchloride we should expect a relatively high selectivity for calcium ions (0.70) and a low one (0.20–0.40) for sodium ions.

2. In using membranes produced on the basis of PVA, piperazine, benzoic acid, and trimezoilchloride we may obtain the selectivity for calcium ions in the limits 0.20–0.30. In the presence of sulfate ions we may expect the selectivity for

sodium of 0.90–0.95, while in the absence of sulfate ions, this selectivity is equal to 0.20–0.30.

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