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Effect of ionic strength on ion exchange equilibrium between cationic membranes and K^+/Na^+, K^+/Li^+ and Na^+/Li^+ binary systems

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ABSTRACT

Ion exchange membranes are receiving considerable attention and are successfully applied for desalination and for treating industrial effluents. They are efficient tools for the concentration or separation of food and pharmaceutical products containing ionic species. Extensive work has been reported on synthesis, characterization, properties and applications of these membranes. In this work ion exchange isotherms for the binary Na^+/K^+, Li^+/K^+, and Li^+/Na^+ were established at various ionic strengths, using CRP cationic membrane. All experiments were carried at 25 °C, by setting the ionic strength in the range of $I = 0.1–1.5\ \text{mol}\cdot\text{l}^{-1}$. All the results given by this membrane were compared with those obtained, in the same conditions, with CMX membrane. For the two membranes, up to ionic strength $1.5\ \text{mol}\cdot\text{l}^{1}$ affinity order was: $K^+ > Na^+ > Li^+$. Selectivity coefficients $K_{Na^+}^{K^+}$, $K_{Li+}^{K^+}$ and $K_{Li^+}^{Na^+}$ for homogenous CMX membrane were greater than those determined for heterogeneous CRP membrane. For low ionic strength till $I = 0.2\ \text{mol}\cdot 1^{1}$, these selectivity coefficients decrease strongly and tend asymptotically to unity for higher values of I. The product of selectivity coefficients $K_{Li^+}^{Na^+}\cdot K_{Na^+}^{K^+}\cdot K_{K^+}^{Li^+}$ were always close to unity.

Keywords: Ion exchange membrane; Selectivity coefficients; Isotherms; Binary system; Ionic strength

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1. Introduction

Ion exchange technology has been widely used for various separation processes such as industrial processing of semiconductors, water softening, and wastewater and groundwater treatment [1–8].

The ion exchange membranes have been mostly used in the solutions containing multi-components, such as electrodialytic concentration of sea water to produce sodium chloride, demineralization of saline water [9]. Ion exchange membrane is actually indispensable for separation of ionic species, especially in environmental protection and clean production. In many applications, ion exchange membrane related processes are in direct competition with other separation techniques, such as distillation, ion exchange and various chromatographic procedures [10]. Since extensive work has been reported in the past decade on synthesis, characterization, properties, selectivity and applications of these membranes [11]. Selectivity coefficient is a fundamental characteristic of ion exchange equilibrium between ionic exchanger and electrolyte solution of two or several ions. Indeed, the experimental determination of the coefficients of the polymers ion exchanger, especially those of the ionic membranes is became necessary. Many attempts were proposed for determination of selectivity coefficients [12]. They determined the selectivity coefficients for three types of cation exchange membranes (CM1, CM2 and Nafion 117), for binary systems (KCl + NaCl, KCl + LiCl and NaCl + LiCl),

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at total concentration 0.1 $mol \cdot l^{-1}$. This work was developed by Poilbout and his coworkers, who determined the selectivity coefficients at different ionic strengths (I) from 0.1 to 1.5 $mol \cdot l^{-1}$ [13]. Miyoshi and his coworkers studied the equilibrium between ion exchange membranes (Selemion and Neosepta) and electrolyte solutions containing (H^+, K^+, Na^+, Ca^{2+}, ...) [14]. It was found that, for monovalent ions, the affinity order was: $H^+ < Na^+ < K^+$.

The aim of the present work is to study the ion exchange equilibrium between CRP cationic membrane and electrolytes solutions of K^+, Na^+, and Li^+ by setting the ionic strength in the range from I = 0.1 to I = 1.5 $mol \cdot 1^{-1}$. All experiments were maintained at constant temperature (25 °C). Selectivity coefficients for the binaries systems: Na^+/K^+, Na^+/Li^+ and K^+/Li^+ were determined. Then, these results were compared to those obtained by CMX membrane in the same conditions [15,16].

Ion analyses were performed by ionic chromatography, coupled to a conductimetric detector.

2. Materials and methods

2.1. Ionic chromatography

At equilibrium ions in solution, for a given membrane, were analyzed by ion chromatography (a Metrohm 761 compact IC ion Chromatography System with conductivity detector, a 125 mm × 4 mm cation exchange column, an eluent of 4 $mmol \cdot l^{-1}$ Tartaric acid and 1 $mmol \cdot l^{-1}$ Dipicolinic acid at 1.0 ml min^{-1}, an injection volume of 20 µl, and a temperature of 25 °C). The feed solutions were prepared from reagent grade chemicals and pure water. Ion exchange chromatography retains analyte molecules on the column based on electrostatic interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge. The ionic compound consisting of the cationic species M^+ and the anionic species B^+ can be retained by the stationary phase. In our work, cation exchange chromatography retains positively charged cations (K^+, Na^+, Li^+ ...) because the stationary phase displays a negatively charged functional group ($-SO_3^-$).

2.2. Membranes characteristics

2.2.1. Membrane structure

Binary ion exchange equilibrium data were obtained with CRP and CMX ion exchange membrane. CRP heterogeneous membrane manufactured by RHONE POULENC (France) can be produced by melting and pressing of a dry ion exchange resin with a granulated polymer (polyvinylochloride) [10]. Another method to prepare heterogeneous membranes is dispersion of the ion exchange resin in a polymer solution.

The CMX is a homogeneous membrane manufactured by Tokuyama Marketed under the brand Neosepta. The preparation of the CMX membrane is made by copolymerization of styrene and divinylbenzene [11,12].

The two membranes are mainly used in electrodialysis and in dialysis. The stabilization of this membrane and the determination of humidity percentage and ion exchange capacity were carried out in our laboratory according to French standard NF X45-200 [17] and presented in previous works [15,16].

2.2.2. Humidity percentage and ion exchange capacity

After the membrane samples (5 × 5 cm^2) were immersed for 24 h in the solution, they were wept between two sheets of blotting paper, weighed and put under emptiness with $MgSO_4$ during 24 h until obtaining a constant weight. The humidity percentage is expressed as the percentage of weight of water sorbed in the membrane over the weight of the dry membrane.

The ion exchange capacity C_E is the number of fixed charges inside the ion exchange membrane per unit weight of dry polymer. The ion exchange capacity is a crucial parameter which affects almost all other membrane properties. The ion exchange capacity is expressed in milliequivalent of fixed groups per gram of dry membrane.

2.3. Ion-exchange isotherms

Ion exchange equilibrium for Na^+/K^+, Li^+/K^+ and Li^+/Na^+ systems using CRP membrane were measured at various ionic strengths from I = 0.1 to 1.5 $mol \cdot l^{-1}$ by setting temperature at 25 °C. The methodology followed in this investigation has already been described in a previous paper [16]. The ion exchange between the solution ($B^{\beta+}$) and the membrane ($A^{\alpha+}$) leads to the following equation:

$$\beta\,\bar{A}^{\alpha+} + \alpha\,B^{\beta+} \rightleftharpoons \beta\,A^{\alpha+} + \alpha\,\bar{B}^{\beta+} \tag{1}$$

where α and β are the charge of the ionic species A and B, respectively, and the bar refers to the membrane phase.

X and $\bar{X}$ are the equivalent fractions of ions A and B in the solution and membrane, respectively defined as:

$$\begin{aligned} X(A) &= \alpha \cdot \frac{[A]}{C_T},\ X(B) = \beta \cdot \frac{[B]}{C_T}; \\ \bar{X}(A) &= \alpha \cdot \frac{[\bar{A}]}{C_E},\ \bar{X}(B) = \beta \cdot \frac{[\bar{B}]}{C_E} \end{aligned} \tag{2}$$

where [i] is the concentration of the ionic species in solution, C_T is the total concentration in the solution phase, $[\bar{i}]$ is the solute concentration in the membrane and C_E is the useful ion exchange capacity of the membrane.

Table 1
Humidity percentage and ion exchange capacity of CMX and CRP membranes

	Membrane CMX	SD (%)	Membrane CRP	SD (%)	References
CE (mmol g^{-1})	1.69	0.8	2.10	2.8	[15,16]
τ_g (%)	23	3.8	32	3.8	[15,16]

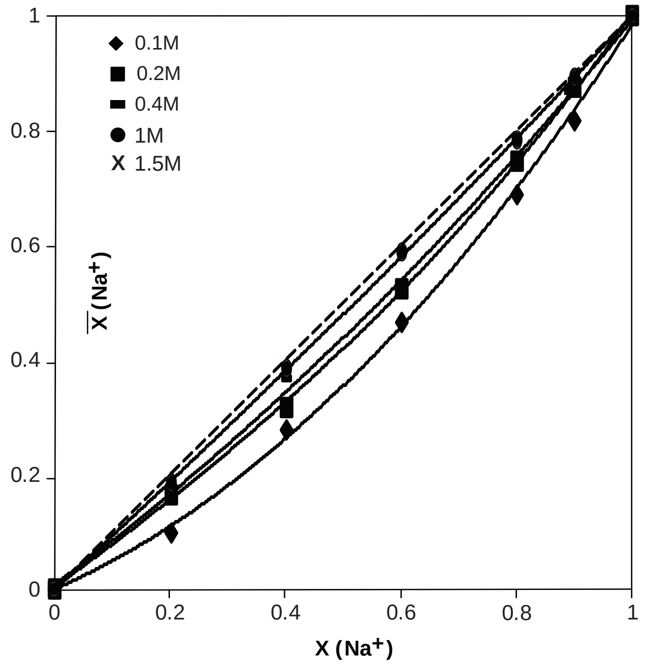

Fig. 1. Isotherms for CRP membrane /Na^+/K^+ system, θ = 25°C and I = 0.1–1.5 mol·l^{-1}.

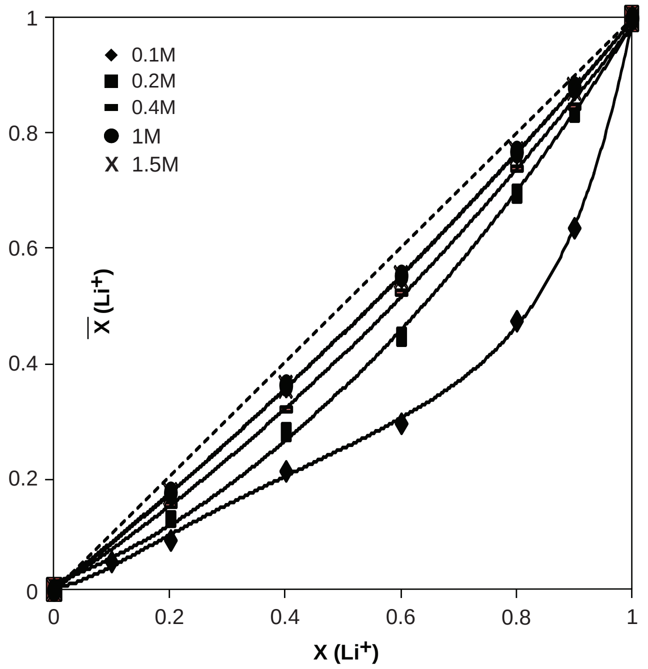

Fig. 2. Isotherms for CRP membrane /Li^+/K^+ system, θ = 25°C and I = 0.1–1.5 mol·l^{-1}.

The membrane phase composition was determined by mass balance from initial and equilibrium compositions of the liquid phase.

For all the systems reported experiments were performed with NO_3^- as counter ion at 25 °C.

3. Results and discussion

Humidity percentage and ion exchange capacity may vary with the membrane samples. Five samples of (5 × 5) cm each were used for the determination of these parameters. Results obtained are presented, with standard deviations SD (%), in Table 1.

3.1. Affinity order

Figs. 1–3 give the ion exchange isotherms for binary systems Na^+/K^+, Li^+/K^+ and Li^+/Na^+ at various ionic strengths I for CRP membrane:

These isotherms make possible the determination of the affinity order of the CRP membrane. The affinity order obtained at various ionic strengths was: $K^+ > Na^+ > Li^+$. This order is often allotted to the fact that the membranes prefer the ion which has lowest molar hydrated volume VH indeed we have [18]:

$$V_H(K^+) = 18.00 < V_H(Na^+) = 51.47 < V_H(Li^+) = 75.00\ cm^3 \cdot mol^{-1}$$

The same order was obtained for CMX membrane [16]. For the same range of ionic strength, Poilbout and his coworkers found the same affinity sequence for CM1, CM2, and Nafion 117 membranes [13]. From Eq. (1) and for monovalent ions, the ion exchange equilibrium should be better described by the following selectivity coefficient, expressed in terms of the molar concentration or in terms of ionic fraction:

$$K_A^B = \frac{\overline{X}(A) \times X(B)}{X(A) \times \overline{X}(B)} = \frac{[\overline{A}] \times [B]}{[A] \times [\overline{B}]} \quad (3)$$

Thus, selectivity coefficient will be given in our study from the quantity of counter-ions in the solution and the

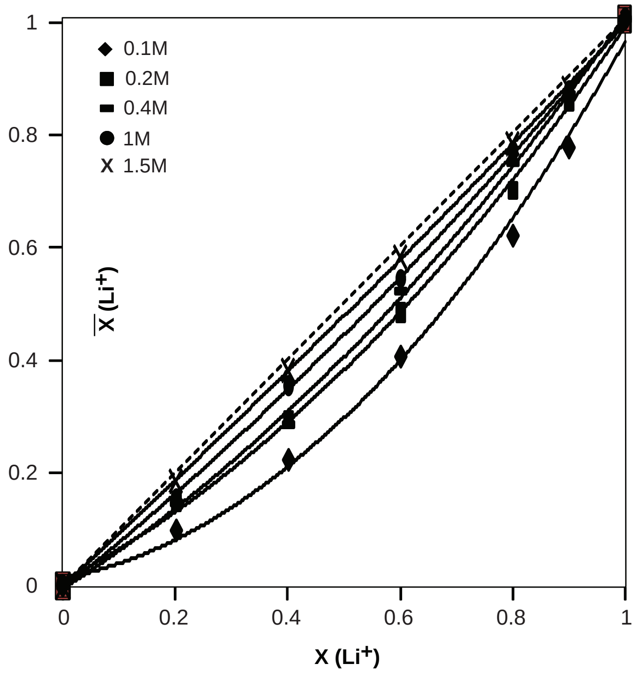

Fig. 3. Isotherms for CRP membrane /Li$^+$/Na$^+$ system, θ = 25 °C and I = 0.1–1.5 mol·l^{-1}.

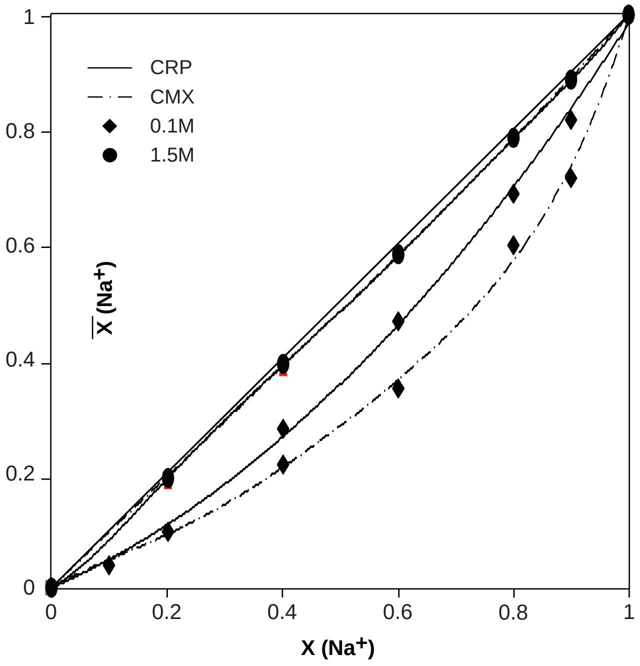

Fig. 4. CRP and CMX selectivity for /Na$^+$/K$^+$ system, at I = 0.1 and I = 1.5 mol·l^{-1}.

membrane. If measurements in solution are easy to realize, the membrane concentrations can be calculated from the defined equations:

$$m \cdot C_E + V \cdot [A]_0 = V \cdot [A] + m \cdot \qquad (4)$$

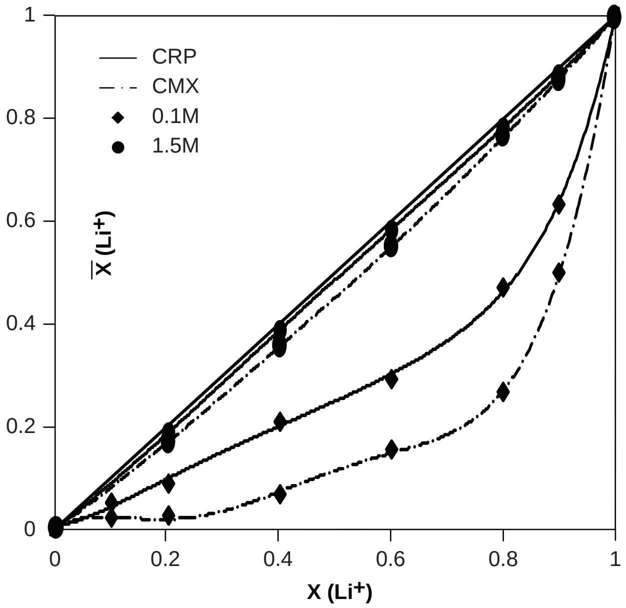

Fig. 5. CRP and CMX selectivity for /Li$^+$/K$^+$ system, at I = 0.1 and I = 1.5 mol·l^{-1}.

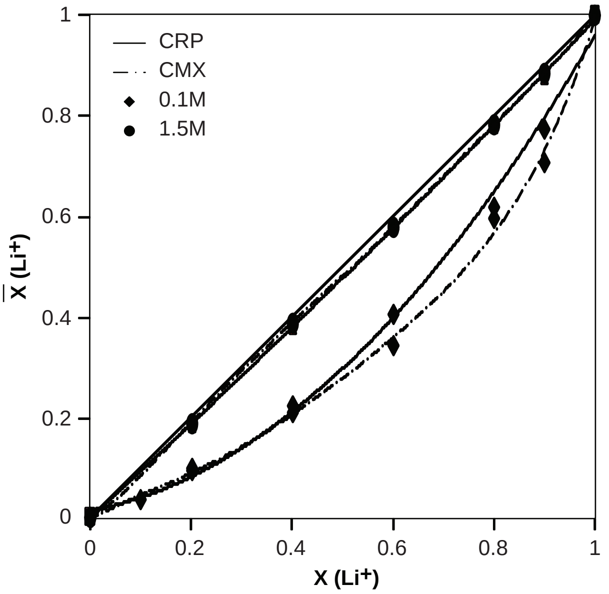

Fig. 6. CRP and CMX selectivity for /Li$^+$/Na$^+$ system, at I = 0.1 and I = 1.5 mol·l^{-1}.

$$V \cdot [B]_0 = V \cdot [B] + m \cdot [\overline{B}] \qquad (5)$$

3.2. Effect of ionic strength on selectivity coefficients

All the results given by CRP heterogeneous membrane were compared with those obtained, in the same conditions, with CMX homogeneous membrane. Figs. 3–6 give to get her ion exchange isotherms for CRP and

Table 2
Selectivity coefficients for Li^+/Na^+ system, membrane CRP, I = 0.1 M at θ = 25 °C

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
$[Li^+]$ mmol · l^{-1}	21.59	41.34	61.65	80.75	90.75
$\overline{[Li^+]}$ meq · g^{-1}	0.21	0.47	0.83	1.28	1.63
$[Na^+]$ mmol · l^{-1}	78.45	58.66	39.09	19.33	9.61
$\overline{[Na^+]}$ meq · g^{-1}	1.89	1.63	1.32	0.77	0.43
$X(Li^+)$	0.2	0.4	0.6	0.8	0.9
$\bar{X}(Li^+)$	0.10	0.22	0.39	0.62	0.77
$K_{Li^+}^{Na^+}$	2.48	2.45	2.50	2.50	2.50

Table 3
Effect of ionic strength on selectivity coefficients values

I (mol · l^{-1})	Membrane CRP						Membrane CMX [16]					
	$K_{Li^+}^{K^+}$	SD(%)	$K_{Li^+}^{Na^+}$	SD(%)	$K_{Na^+}^{K^+}$	SD(%)	$K_{Li^+}^{K^+}$	SD(%)	$K_{Li^+}^{Na^+}$	SD(%)	$K_{Na^+}^{K^+}$	SD(%)
0.1	4.0	1.14	2.5	2.19	1.7	2.44	9.8	2.04	3.3	2.91	2.7	3.28
0.2	1.8	1.14	1.6	2.64	1.3	2.05	2.2	2.68	1.7	2.23	1.6	3.57
0.4	1.5	2.26	1.3	2.19	1.3	2.07	1.9	2.38	1.36	1.87	1.5	3.11
1	1.2	2.23	1.2	3.03	1.1	0.84	1.8	2.68	1.3	2.73	1.3	2.83
1.5	1.2	2.38	1.1	2.68	1.1	0.71	1.1	2.68	1.1	3.03	1.1	3.57

SD (%): standard deviation.

Table 4
Values of selectivity coefficients product

I (mol · l^{-1})	Membrane CRP	Membrane CMX [16]
	$K_{Li^+}^{Na^+} \cdot K_{Na^+}^{K^+} \cdot K_{K^+}^{Li^+}$	$K_{Li^+}^{Na^+} \cdot K_{Na^+}^{K^+} \cdot K_{K^+}^{Li^+}$
0.1	1.0	0.9
0.2	1.1	1.2
0.4	1.1	1.1
1	1.1	0.9
1.5	1.0	1.1

CMX membrane for studied binary systems at I = 0.1 and at I = 1.5 mol · l^{-1}.

It appears from Figs. 4–6 that CMX homogeneous membranes have a better selectivity than CRP heterogeneous membrane. This difference is important at low ionic strength.

The selectivity coefficients were calculated starting from Eq. (3), in Table 2 details were given to show how selectivity coefficients were calculated, tacking the example of Li^+/Na^+ system for I = 0.1 M.

In Table 3 results obtained in previous work [16] for CMX/(K^+, Na^+, Li^+) systems are given.

The results shown in Table 2 confirm that selectivity coefficients decrease with increasing ionic strength and tend to the unity. This result was obtained for CM1, CM2 and Nafion 117 membranes [13]. The loss of selectivity with increasing ionic strength is mainly due to salt leakage in the membrane with increasing ionic concentration as described by Helfferich [18].

However selectivity coefficients at lower ionic strength are higher for the Homogeneous CMX membrane compared to heterogeneous CRP membrane. A possible reason could be higher water uptake in the CRP membrane, as shown in Table 4, lowering its selectivity values. For the two membranes the product of selectivity coefficients $K_{Li^+}^{Na^+} \cdot K_{Na^+}^{K^+} \cdot K_{K^+}^{Li^+}$ is close to theoretical value of unity at different studied ionic strengths, showing the accuracy of our experimental results (Table 3).

4. Conclusions

Isotherms and selectivity coefficients for the binary systems Na^+/K^+, Li^+/K^+, and Li^+/Na^+ were determined at various ionic strengths for CRP membrane and results were compared to those obtained in previous work with CMX membrane. For the two CRP and CMX membranes, up to ionic strength 1.5 mol · l^{-1} affinity order for Na^+, K^+ and Li^+ cations was $K^+ > Na^+ > Li^+$. Potassium is more preferred by these membranes over any other ccording to its small hydrated volume. Selectivity coefficients $K_{Li^+}^{Na^+}$, $K_{Na^+}^{K^+}$ and $K_{Li^+}^{K^+}$ were determined at 25 °C. The obtained results show that the selectivity coefficients decreases with increasing ionic strength and tend asymptotically to the unity for high values of I. The product of selectivity coefficients $K_{Li^+}^{Na^+} \cdot K_{Na^+}^{K^+} \cdot K_{K^+}^{Li^+}$ is close to unity at different studied ionic strengths. Homogenous CMX membrane gives selectivity coefficients greater than those obtained by heterogeneous CRP membrane.

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