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Determination of the selectivity coefficient of the CMX cationic membrane at various ionic strengths

Ch. Hannachi*[a], M. Ben Sik Ali[b], B. Hamrouni[a]
[a]*UR Traitement et Dessalement des Eaux, Faculté des sciences de Tunis, 2092 Manar II, Tunisia*
Tel/Fax +216 (71) 871-282; email: chiraz_hannach@yahoo.fr.
[b]*Laboratoire Eau et Technologies Membranaires, Pôle Technologique de Bordj-Cédria, BP 273, 8020 Soliman, Tunisia*

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ABSTRACT

Equilibrium between CMX cationic membrane and solutions of cations at various ionic strengths were studied and the affinity order for different counter-ions was made. Membrane water content and ion exchange capacity were determined. The equilibrating solutions were equimolar mixtures of alkaline nitrates of potassium, sodium and calcium and the ionic strength (I) was varied from 0.1 to 1.5 mol.L^{-1}. All experiments were maintained at constant temperature (25°C). Adsorption isotherms for the five binary systems: Na^+/K^+, Li^+/K^+, Li^+/Na^+, Na^+/Ca^{2+} and K^+/Ca^{2+} were studied. The affinity order observed was: $K^+ > Ca^{2+} > Na^+ > Li^+$. Selectivity coefficients $K_{Na^+}^{K^+}$, $K_{Li^+}^{K^+}$, $K_{Li^+}^{Na^+}$, $K_{2Na^+}^{Ca^{2+}}$ and $K_{2K^+}^{Ca^{2+}}$ were determined at 25°C. The selectivity coefficients decreases with increasing ionic strength for low values of I and tended asymptotically to the unity for high values of *I*.

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

1. Introduction

Separation membranes have become essential materials not only in industries, but also in daily human life. Thus, various membranes have been developed: membranes for reverse osmosis, nanofiltration, ultrafiltration, microfiltration, electrodialysis, pervaporation processes, ion exchange membranes, membranes for medical use such as an artificial kidney, etc. [1–3].

Since their advent, synthetic ion exchange materials have been the object of considerable study by numerous investigators. Ion exchange membranes have been mostly used in the solutions containing multi-components (K^+, Na^+, Li^+) such as electrodialytic concentration of seawater to produce sodium chloride, demineralization of saline water, desalination of cheese whey solutions, etc. [4].

Selectivity coefficient is a fundamental characteristic of ion exchange equilibrium for any ion exchanger polymer placed in a mixture of two or several electrolytes. Indeed, the experimental determination of the coefficients of the polymers ion exchanger, especially those of the ionic membranes, has become necessary. Many attempts have been made for determination of the selectivity coefficient. Bessière et al. [5] determined the selectivity coefficients for three types of cation exchange membranes (CM1, CM2 and Nafion 117) at total concentration 0.1 mol.L^{-1}. Miyoshi et al. [6] determined the selectivity coefficient of two ion exchange membranes (Selemion and Neosepta). Poilbout et al. [7] studied the ion exchange equilibrium between a cationic ion exchange membrane and electrolyte solutions, the ionic strength was varied from 0.1 to 1.5 mol.L^{-1} at 25°C.

The aim of the present work is to study the binary ion exchange equilibrium between the CMX cationic

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* Corresponding author.

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membrane and electrolyte solutions (K^+, Na^+, Ca^{2+} and Li^+). The selectivity order and the values of the selectivity coefficient at different ionic strengths were determined. All experiments were maintained at a constant temperature (25°C). Ion analyses were performed by ionic chromatography coupled to a conductimetric detector.

2. Materials and methods

2.1. Ionic chromatography

Cations were determined by ionic chromatography using a Metrohm 761 compact IC with conductivity detector and chemical suppression. The feed solutions were prepared from reagent grade chemicals and pure water.

2.2. Membrane characteristics

Ion exchange equilibrium data were obtained for the CMX cationic membrane. The manufacture data were completed by the determination of the water content and the ion exchange capacity of the membrane.

Before any exchange measurements were made, these membrane properties (water content (τ_g) and ion exchange capacity (C_E)) were determined according to the French standard NF X45-200 [8]. All experiments were performed at room temperature $\theta = 25°C$.

2.2.1. Water content

Each membrane sample (5 × 5 cm) under specific ionic form was immersed during 4 h of agitation in known ionic solution. At the equilibrium, the membrane was rapidly dried (m_h is the humid membrane mass) and put under emptiness with $MgSO_4$ during 24 h until obtaining a constant mass (m_s is the dried membrane mass). The water content was calculated by the following equation:

$$\tau_g = \frac{m_h - m_s}{m_h} \times 100 \quad (1)$$

2.2.2. Ion exchange capacity

Experiences were made on pieces of a membrane (5 × 5 cm) in the form of A immersed in 1 M solution of B. At equilibrium, the quantity n of A leached in solution linked to the dried mass m of the membrane led to the ion exchange capacity C_E:

$$C_E = \frac{n}{m} \quad (2)$$

2.3. Ion exchange isotherms

The CMX membrane in the form of A equilibrated in a solution of B led to the following equilibrium equation:

$$\beta\bar{A}^{\alpha+} + \alpha B^{\beta+} \rightleftharpoons \beta A^{\alpha+} + \alpha\bar{B}^{\beta+} \quad (3)$$

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

The equivalent ionic fraction $X(i)$ and $\bar{X}(i)$ for a binary system can be introduced as:

$$X(A) = \alpha\frac{[A]}{C_T},\ X(B) = \beta\frac{[B]}{C_T}$$
$$\bar{X}(A) = \alpha\frac{[\bar{A}]}{C_E},\ \bar{X}(B) = \beta\frac{[\bar{B}]}{C_E} \quad (4)$$

where, $[i]$ is the concentration of the ionic species i in solution (mmol.L^{-1}), C_T — the total concentration in the solution phase (mmol.L^{-1}), $[\bar{i}]$ — the solute i concentration in the membrane (mmol.g^{-1}), C_E — ion exchange capacity of the membrane (mmol.g^{-1}).

At equilibrium, the concentrations of various ions present in the solution were determined by ionic chromatography and the specific amounts of ions on the membrane during the experiments were calculated using the following equations:

$$C_T = [A] + [B] \quad (5)$$

$$C_E = [\bar{A}] + [\bar{B}] \quad (6)$$

$$VC_T = V[B] + m_s[\bar{B}] \quad (7)$$

$$m_sC_E + V[A]_0 = m_s[\bar{A}] + V[A] \quad (8)$$

3. Results and discussion

Some characteristic parameters of the CMX membrane are presented in Table 1.

Table 1
Some parameters of the CMX membrane

Parameter		Reference
C_E, mmol.g^{-1}	1.69	This study
τ_g, %	23	This study
e, μm	175	[9]
Density	1.26	[9]

3.1. Ion exchange isotherms

The isotherms of binary ion exchange were established for the couples Na^+/K^+, Li^+/K^+, Li^+/Na^+, Na^+/Ca^{2+} and K^+/Ca^{2+}. For all the systems reported experiments were performed with NO_3^- as non exchanging anion at 25°C.

Figs. 1–5 give the adsorption isotherms for the studied binary systems at $I = 0.1$ mol.L^{-1}.

These isotherms make possible the determination of the affinity order of these ions for the CMX membrane.

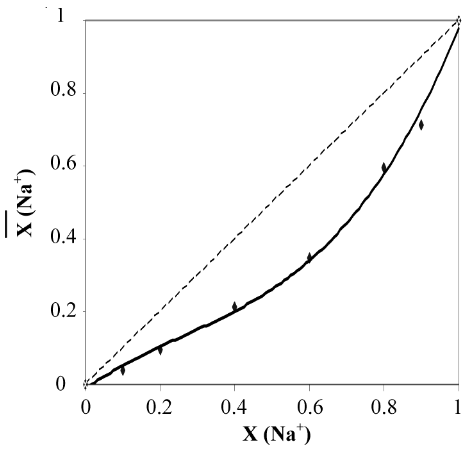

Fig. 1. Isotherm for the system Na$^+$/K$^+$, θ = 25°C and I = 0.1 mol.L^{-1}.

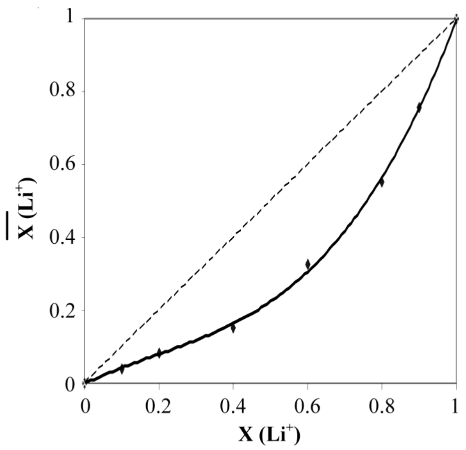

Fig. 2. Isotherm for the system Li$^+$/Na$^+$, θ = 25°C and I = 0.1 mol.L^{-1}.

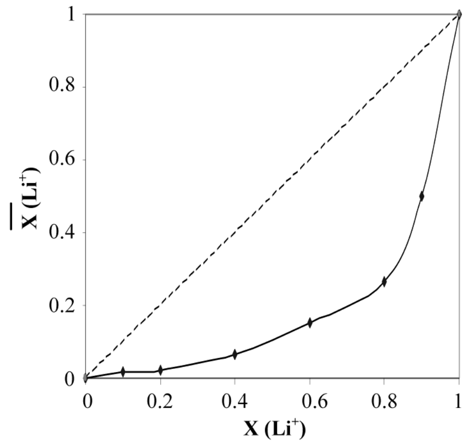

Fig. 3. Isotherm for the system Li$^+$/K$^+$, θ = 25°C and I = 0.1 mol.L^{-1}.

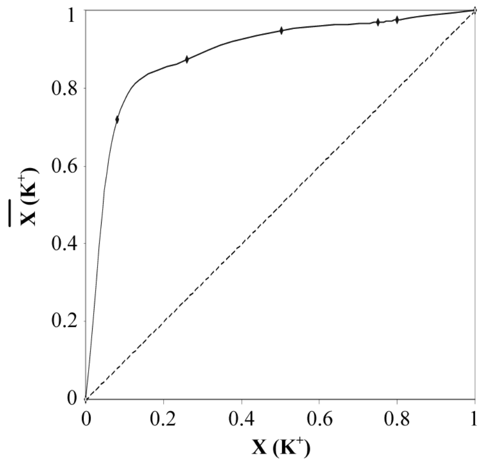

Fig. 4. Isotherm for the system K$^+$/Ca^{2+}, θ = 25 °C and I = 0.1 mol.L^{-1}.

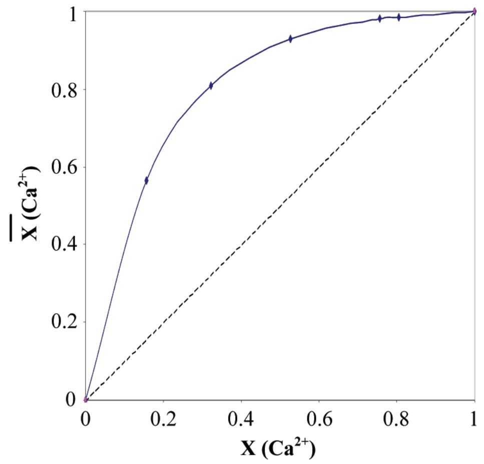

Fig. 5. Isotherm for the system Na$^+$/Ca^{2+}, θ = 25°C and I = 0.1 mol.L^{-1}.

The order of the membrane preference for the studied cations at C_T = 0.1 mol.L^{-1} was K$^+$ > Ca^{2+} > Na$^+$ > Li$^+$

This order K$^+$ > Na$^+$ > Li$^+$ may be explained [10–16] by the fact that the membrane has preference for the smallest ions according to their hydrated ion radius, r_{ih}, shown in Table 2.

Table 2
Values of the hydrated ion radius [17].

Ions	r_{ih} (Å)	Z/r_{ih}
Li$^+$	7.3	0.14
Na$^+$	5.6	0.18
Ca^{2+}	9.6	0.21
K$^+$	3.8	0.26

The same order $K^+ > Na^+$ was found by Bessière et al. [5] for the three types of membranes (CM1, CM2 and Nafion 117) at total concentration equal to 0.1 mol.L^{-1}. In general divalent ions are always, in dilute solutions, more preferred by the membrane than monovalent ions. This is verified for Ca^{2+}, Na^+ and Li^+ ($Ca^{2+} > Na^+ > Li^+$) not for Ca^{2+} and K^+. This behavior is well known for the ion exchange resins [18,19]. The observed selectivity order $K^+ > Ca^{2+}$ constitute an anomalously high selectivity for potassium relative to calcium. This may be explained by comparing the ions ratio Z/r_{ih}, for which the order is the following: Z/r_{ih} (K^+) > Z/r_{ih} (Ca^{2+}) > Z/r_{ih} (Na^+)> Z/r_{ih} (Li^+). This observed selectivity order was confirmed by Gregor et al. [20] and Reichenberg et al. [21]. They found by using an acid membrane polystyrene sulphonic and solutions of electrolytes containing the ions Ca^{2+}, Na^+ and K^+ whose order of affinity was $K^+ > Ca^{2+} > Na^+$at 0.1 mol.L^{-1}.

3.2. *Effect of ionic strength*

The effect of ionic strength was studied for the three binary systems: Na^+/K^+, Li^+/K^+ and Li^+/Na^+. Ionic strength was varied between 0.1 mol.L^{-1} and 1.5 mol.L^{-1}. Figs. 6–8 give the adsorption isotherms for the studied binary systems at experimental conditions.

The obtained results show that when the ionic strength increases the affinity of the ion exchanger membrane decreases. This behaviour well known for ion exchange resin was observed for ion exchange membranes [7,22].

3.3. *Selectivity coefficients*

The selectivity coefficient is a fundmental characteristic of equilibrium of an ionic membrane when placed in a mixture of two or several dilute electrolytes. The general expression used for this coefficient is:

$$K_A^B = \frac{[\overline{A}]^\beta \cdot [B]^\alpha}{[A]^\beta \cdot [\overline{B}]^\alpha} \qquad (9)$$

Thus, selectivity coefficient will be given in our study from the quantity of counter-ions in the solution and the membrane. If measurements in the solution are easy to realize, the membrane concentrations are not directly accessible and require various preliminary operations. Miyoshi et al. [6] determined the selectivity coefficient for a Selemion membrane for various counter-ions.

Selectivity coefficients for the binary systems Na^+/K^+, Li^+/K^+, Li^+/Na^+, Na^+/Ca^{2+} and K^+/Ca^{2+} were calculated from experimentally measured concentrations as described below. An example of selectivity coefficient calculation is given for the case of the binary system Na^+/K^+ at the ionic strength of 0.1 mol.L^{-1} and θ = 25°C is given in Table 3.

The selectivity coefficients were calculated starting from the following relations:

$$\overline{K}^+ + Na^+ \rightleftharpoons K^+ + \overline{Na}^+,\ K_{K^+}^{Na^+} = \frac{[K^+]\cdot[\overline{Na}^+]}{[\overline{K}^+]\cdot[Na^+]} \qquad (10)$$

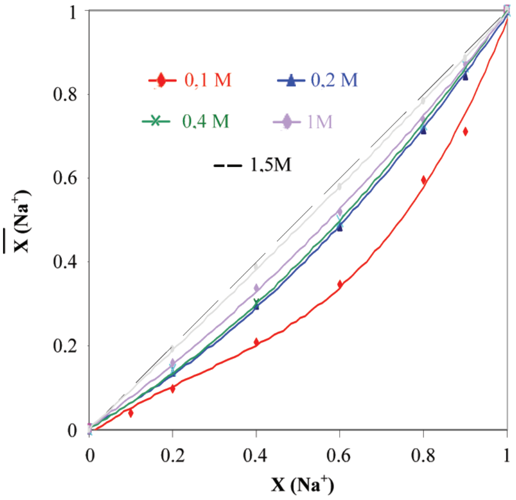

Fig. 6. Isotherms for the system Na^+/K^+, θ = 25°C and *I* = 0.1–1.5 mol.L^{-1}

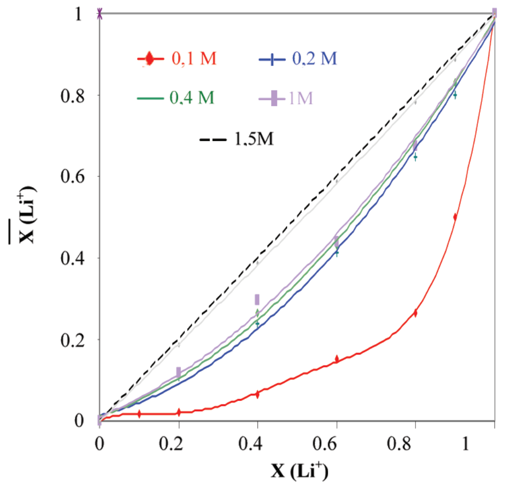

Fig. 7. Isotherms for the system Li^+/K^+, θ = 25°C and *I* = 0.1–1.5 mol.L^{-1}.

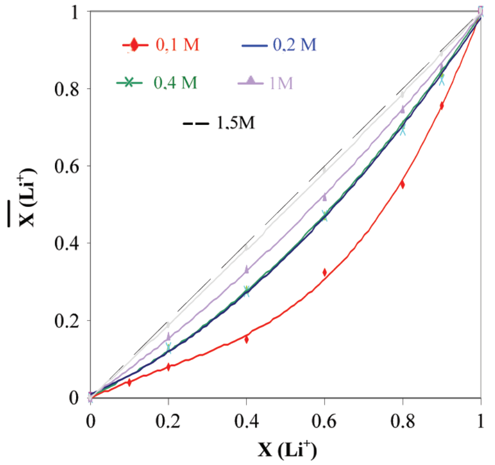

Fig. 8. Isotherms for the system Li^+/Na^+, θ = 25°C and *I* = 0.1–1.5 mol.L^{-1}.

Table 3
Selectivity coefficient K^{K+}_{Na+} at ionic strength 0.1 mol.L^{-1} and θ = 25°C

Sample	[Na$^+$] (mol.L^{-1})	[K$^+$] (mol.L^{-1})	$[\overline{Na}^+]$ meq.g^{-1}	$[\bar{K}^+]$ meq.g^{-1}	K^{K+}_{Na+}
1	0.090	0.0097	1.125	0.375	3.10
2	0.075	0.025	0.750	0.75	3.00
3	0.062	0.0375	0.465	1.035	3.72
4	0.031	0.069	0.251	1.249	2.23
5	0.013	0.086	0.126	1.374	1.64

$$\overline{Li}^+ + K^+ \rightleftharpoons Li^+ + \bar{K}^+,\ K^{Na^+}_{K^+} = \frac{[Li^+]\cdot[\bar{K}^+]}{[\overline{Li}^+]\cdot[K^+]} \tag{11}$$

$$\overline{Li}^+ + Na^+ \rightleftharpoons Li^+ + \overline{Na}^+,\ K^{Na^+}_{K^+} = \frac{[Li^+]\cdot[\overline{Na}^+]}{[\overline{Li}^+]\cdot[Na^+]} \tag{12}$$

$$2\bar{K}^+ + Ca^{2+} \rightleftharpoons 2K^+ + \overline{Ca}^{2+},\ K^{Ca^{2+}}_{2K^+} = \frac{[K^+]^2\cdot[\overline{Ca}^{2+}]}{[\bar{K}^+]^2\cdot[Ca^{2+}]} \tag{13}$$

$$2\overline{Na}^+ + Ca^{2+} \rightleftharpoons 2Na^+ + \overline{Ca}^{2+},\ K^{Ca^{2+}}_{2Na^+} = \frac{[Na^+]^2\cdot[Ca^{2+}]}{[\overline{Na}^+]^2\cdot[Ca^{2+}]} \tag{14}$$

The results are represented in Tables 4 and 5.

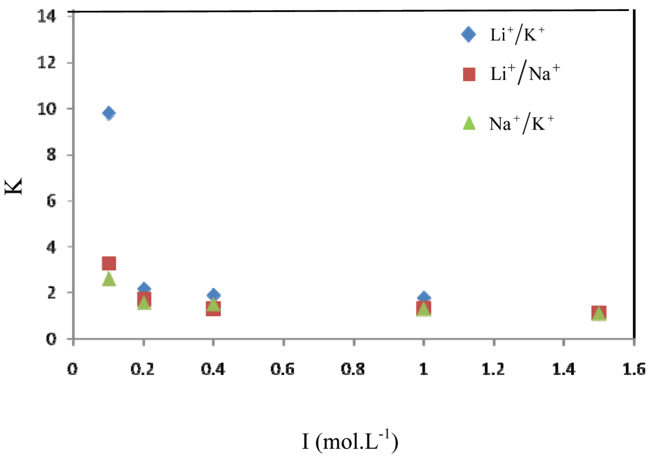

Fig. 9. Variation of the selectivity coefficient for the CMX membrane according to ionic strength (*I*).

The effect of ionic strength on the selectivity coefficients at 25°C is shown in Fig. 9. The influence of the ionic strength seems to be important for low ionic concentration where selectivity coefficients decrease and tend to the unity for high values of *I* (greater than 0.4 mol.L^{-1}). The order for the three ion exchange systems is:

$$K^{K^+}_{Li^+} > K^{Na^+}_{Li^+} > K^{K^+}_{Na^+}$$

Table 4
Experimental values of the selectivity coefficient for the CMX membranes and for the five binary systems at 0.1 mol.L^{-1}

$K^{K^+}_{Li^+}$	$K^{Na^+}_{Li^+}$	$K^{K^+}_{Na^+}$	$K^{Ca^{2+}}_{2Na^+}$	$K^{Ca^{2+}}_{2K^+}$
9.8	3.3	2.7	3.2	0.3

Table 5
The average experimental values of the selectivity coefficient determined for the CMX membranes and for the binary systems at various ionic strengths

I (mol.L^{-1})	$K^{K^+}_{Li^+}$	$K^{Na^+}_{Li^+}$	$K^{K^+}_{Na^+}$	$K^{Na^+}_{Li^+}\cdot K^{K^+}_{Na^+}\cdot K^{Li^+}_{K^+}$
0.1	9.8	3.3	2.7	0.9
0.2	2.2	1.7	1.6	1.2
0.4	1.9	1.3	1.5	1.1
1	1.8	1.3	1.3	0.9
1.5	1.1	1.1	1.1	1.1

4. Conclusion

Adsorption isotherms were established for the binary systems: Na$^+$/K$^+$, Li$^+$/K$^+$, Li$^+$/Na$^+$, Na$^+$/Ca^{2+} and K$^+$/Ca^{2+} at C_T = 0.1 mol.L^{-1} and θ = 25°C. The affinity order for the CMX membrane is: K$^+$ > Ca^{2+} > Na$^+$ > Li$^+$. Selectivity coefficients $K^{K^+}_{Na^+}$, $K^{K^+}_{Li^+}$, $K^{Ca^{2+}}_{2Na^+}$, $K^{Ca^{2+}}_{2K^+}$ and $K^{Li^+}_{Na^+}$ were determined. The effect of ionic strength was studied for the three binary systems: Na$^+$/K$^+$, Li$^+$/K$^+$, and Li$^+$/Na$^+$ in the range *I* = 0.1 mol.L^{-1}–0.5 M. The calculation of selectivity coefficients $K^{Na^+}_{K^+}$, $K^{Li^+}_{K^+}$ and $K^{Li^+}_{Na^+}$ were determined. The affinity order of the membrane did not change but the affinity decreased when the ionic strength increased. The influence of the ionic strength is important for low ionic concentrations, and selectivity coefficients tend asymptotically to the unity for high values of *I*.

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