Water transport in bi-ionic systems: theoretical treatment and effect on the bi-ionic potential

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In a previous paper, we have proposed a new experimental method for measuring the water flow and the convection velocity, v_M, in the case of a bi-ionic system. In the present paper, we propose analytical and numerical treatments to evaluate the contribution (ΔBIP) of the measured convection velocities to the bi-ionic potential values. These theoretical treatments are based on the pseudo-thermodynamic equation and show a linear relationship between ΔBIP and v_M. The ΔBIP values were less than 0.8 mV for concentrations less than 2.0 M. This represents about 4–6% of the experimental bi-ionic potential values obtained with a high selective ion exchange membrane (CM2). The convection velocity v_M and its contribution to the BIP values are theoretically more important for less selective membranes.

Transport d'eau dans les systèmes bi-ioniques: traitement théorique et effet sur le potentiel bi-ionique. Dans un article précédent, nous avons proposé une méthode expérimentale pour mesurer le flux d'eau et la vitesse de convection v_M dans le cas d'un système bi-ionique. Dans le présent article, nous proposons des traitements analytiques et numériques pour évaluer la contribution, ΔBIP, des vitesses de convection mesurées sur les valeurs du potentiel bi-ionique. Ces traitements théoriques sont basés sur l'équation pseudo-thermodynamique et montrent une relation linéaire entre ΔBIP et v_M. Les valeurs de ΔBIP sont en dessous de 0.8 mV pour des concentrations inférieures à 2.0 M. Ceci représente environ 4–6% des valeurs expérimentales du potentiel bi-ionique obtenues avec une membrane échangeuse d'ions très sélective (CM2). La vitesse de convection v_M et ses contributions aux valeurs du BIP sont théoriquement plus importantes pour des membranes moins sélectives.

A bi-ionic system (BIS) contains two electrolyte solutions, AY and BY, at the same concentration, C_0, with Y as a co-ion, and which are separated by an ion-exchange membrane (IEM):

$$\text{AY}(C_0) \mid \text{IEM} \mid \text{BY}(C_0)$$

The electric potential difference between the two solutions is called the bi-ionic potential (BIP). Until 1980, the only process considered to occur in a BIS was the interdiffusion of the two counter ions, A and B, within the membrane and the two diffusion boundary layers (DBL).[1] In 1995, Guirao *et al.*[2] proposed a theoretical treatment taking into account the co-ion flux for solving the Nernst–Planck equations corresponding to a BIS. Our experimental results[3] were in good agreement with the predictions of Guirao *et al.* They confirmed, for the first time, the existence of a maximum in the BIP *vs.* C_0 curves. Guirao *et al.* supposed, without any experimental justification, that the water flow through the ion-exchange membrane is null, that the membrane selectivity coefficient is equal to unity and that the membrane affinity coefficient is equal to one.

In a previous paper,[4] we have shown that water flow across an ion-exchange membrane, used in a BIS, is not negligible. We have also proposed a simple and accurate method to measure this flow and then compute the convection velocity, v_M, for a given BIS at a given concentration $C_0 \in [10^{-1}$–$4.0]$ M. The determination of v_M can be done for two membrane models. In the first, homogeneous model, the total membrane surface has been considered. However, in the second case, the heterogeneous model, only the effective cross-ionic transfer surface has been taken into account. Note that the proposed method can be generalized to some other systems and procedures: multi-ionic systems,[5] osmosis,[6] *etc.*

In this paper, we will focus our study on the effect of the water flow on the BIP values. We will first present a theoretical treatment permitting the evaluation of this effect, then use the pseudo-thermodynamic equation[5] to take into account the contribution of the convection velocity to the ionic fluxes, while considering the membrane selectivity and affinity coefficients to be equal to one. This assumption is to simplify our treatment. However, we are carrying out experimental measurements of these two coefficients and evaluating their influence on the interdiffusion process in a bi-ionic system.

Theoretical evaluation of the water flux effect on the BIP

In an ion-exchange membrane, the coupling between the water flux and the ion fluxes cannot be neglected. In order to take into account this phenomenon, some authors introduce a corrective term in the Nernst–Planck equation. The obtained equation is called pseudo-thermodynamic, in which the overall flux J_i of an arbitrary species i, in the direction x, is composed of three additive terms: the diffusion flux $(J_i)_{diff}$ caused by the chemical potential gradient of the species, the electric transference $(J_i)_{el}$ driven by the electric potential gradient and the transfer $(J_i)_{con}$ driven by convection.[5] The diffusion flux is given by:

$$J_i = -D_i \left\{ \text{grad}(C_i) + C_i \, \text{grad}[\ln(\gamma_i)] + z_i C_i \frac{F}{RT} \, \text{grad}(\phi) \right\} + C_i v_M \quad (1)$$

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where v_M is the velocity of the gravity center of the species i relative to a fixed reference: the macromolecular matrix of the ion-exchanger.

Note that Helfferich[5] and Schlögl[7] have linked the convection velocity v_M to the electric potential and pressure gradients. Helfferich found:

$$v_M = \frac{zFX}{\rho_0 \varepsilon} \cdot \text{grad } \phi$$

and Schlögl obtained:

$$v_M = \frac{1}{\rho_0} \cdot \left(\frac{zFX}{\varepsilon} \text{ grad } \phi - \text{grad } P \right)$$

where z is the ion-exchange fixed charges sign, X the fixed charges molarity, ε the exchanger porosity, ρ_0 the hydraulic specific resistance of the porous exchanger and P the pressure within the exchanger.

The experimental verification of these two equations is very difficult, especially in the case of the IEM, because we cannot know all the parameters ε, ρ_0 and P with good accuracy.

The direct measurement of v_M, as proposed in a previous paper,[4] remains the better method of its determination.

Analytical resolution of the pseudo-thermodynamic equations

Fig. 1 shows the bi-ionic system studied by Inenga and Yoschida.[1] The transport is considered in the x direction, from $-\delta$ to $d + \delta$, and all ions are monovalent. The fixed charge concentration of the cation-exchange membrane is denoted by X and the DBL thickness δ is assumed to be dictated only by the hydrodynamics conditions, following the Nernst layer model.[5,8,9]

The pseudo-thermodynamic equation can be written as:

$$j_i = \frac{J_i}{D_i} = -\left(\frac{dC_i}{dx} + z_i C_i \frac{F}{RT} \frac{d\phi}{dx} \right) + \zeta_i v_M \quad (2)$$

where $\zeta_i = C_i/D_i$ (D_i is the diffusion coefficient of the species i) and γ_i is considered to be equal to unity (note that we have taken the affinity and selectivity coefficients equal to one).

Writing eqn. (2) for the three ions (A^+, B^+ and Y^-) and combining them gives:

$$j_A + j_B + j_Y = -\frac{d(C_A + C_B + C_Y)}{dx} + \frac{F}{RT} \frac{d\phi}{dx} (C_Y - C_B - C_A)$$
$$+ v_M(\zeta_A + \zeta_B + \zeta_Y) \quad (3)$$

Noting that $\Gamma = (j_A + j_B - j_Y)/(j_A + j_B + j_Y)$ and adding $(1 - \Gamma)/2$ times eqn. (3) to the eqn. (2), we obtain:

$$0 = -(1 - \Gamma) \frac{dC_Y}{dx} - \frac{X}{2}(1 - \Gamma) \frac{F}{RT} \frac{d\phi}{dx}$$
$$+ v_M \frac{1 - \Gamma}{2} (\zeta_A + \zeta_B + \zeta_Y)$$
$$+ \frac{dC_Y}{dx} - C_Y \frac{F}{RT} \frac{d\phi}{dx} - \zeta_Y v_M \quad (4)$$

After rearrangement of this equation, we obtain:

$$\frac{F}{RT} \frac{d\phi}{dx} = \Gamma \frac{C_Y}{C_Y + X(1 - \Gamma)/2}$$
$$+ v_M \frac{(1 - \Gamma)(\zeta_A + \zeta_B + \zeta_Y)/2 - \zeta_Y}{C_Y + X(1 - \Gamma)/2}$$

Its integration leads to:

$$\psi(d) - \psi(0) = \Gamma \ln \left\{ \frac{C_Y(d) + X(1 - \Gamma)/2}{C_Y(0) + X(1 - \Gamma)/2} \right\}$$
$$+ v_M \int_0^d \frac{(1 - \Gamma)(\zeta_A + \zeta_B + \zeta_Y)/2 - \zeta_Y}{C_Y + X(1 - \Gamma)/2} dx \quad (5)$$
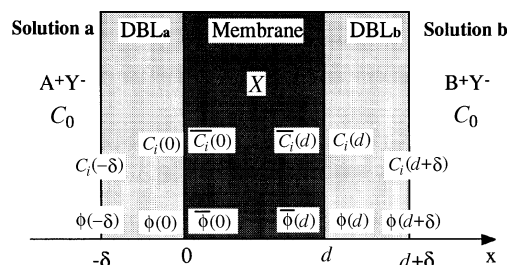

Fig. 1 Schematic view of the bi-ionic system under study

where $\psi = \phi F/RT$.

A similar equation can be obtained for the DBL. The results are similar to those obtained within the membrane except that the fixed charges concentration, X, is null. For DBLa, we get:

$$\psi(0) - \psi(-\delta) = \Gamma \ln \left\{ \frac{C_Y(0)}{C_Y(-\delta)} \right\}$$
$$+ v_M \int_{-\delta}^0 \frac{(1 - \Gamma)(\zeta_A + \zeta_B + \zeta_Y)/2 - \zeta_Y}{C_Y} dx \quad (6a)$$

and for DBLb:

$$\psi(d + \delta) - \psi(d) = \Gamma \ln \left\{ \frac{C_Y(d + \delta)}{C_Y(d)} \right\}$$
$$+ v_M \int_d^{d+\delta} \frac{(1 - \Gamma)(\zeta_A + \zeta_B + \zeta_Y)/2 - \zeta_Y}{C_Y} dx \quad (6b)$$

Taking into account the Donnan potentials at the two membrane/DBL interfaces, we obtain:

$$BIP(v_M \neq 0) = BIP(v_M = 0)$$
$$+ v_M\{I_0^d(X) + I_d^{d+\delta}(X = 0) + I_{-\delta}^0(X = 0)\} \quad (7)$$

where

$$I_a^b(X) = \int_a^b \frac{(1 - \Gamma)(\zeta_A + \zeta_B + \zeta_Y)/2 - \zeta_Y}{C_Y + X(1 - \Gamma)/2} dx$$

For a given C_0, and if we neglect the variations of each integral with the convection velocity v_M, we can suppose the sum of the three integrals in eqn. (7) to be constant, so the BIP varies linearly with v_M. Knowledge of this convection velocity allows us to evaluate the error on the BIP value when the water flow is neglected.

Numerical resolution of the pseudo-thermodynamic equations

Eqn. (1) can be written in the following simplified form:

$$J_i = -D_i \left(\frac{dC_i}{dx} + z_i C_i \frac{F}{RT} \frac{d\psi}{dx} \right) + C_i v_M$$

For the three ions A^+, B^+ and Y^-, present in the membrane, this equation leads to the system of equations:

$$J_A = -\overline{D_A} \left(\frac{d\overline{C_A}}{dx} + \overline{C_A} \frac{F}{RT} \frac{d\overline{\psi}}{dx} \right) + \overline{C_A} v_M$$

$$J_B = -\overline{D_B} \left(\frac{d\overline{C_B}}{dx} + \overline{C_B} \frac{F}{RT} \frac{d\overline{\psi}}{dx} \right) + \overline{C_B} v_M$$

$$J_Y = -\overline{D_Y} \left(\frac{d\overline{C_Y}}{dx} - \overline{C_Y} \frac{F}{RT} \frac{d\overline{\psi}}{dx} \right) + \overline{C_Y} v_M$$

in which the overbar denotes the membrane parameters.

Combined with the electroneutrality equation and the condition of zero electric current we obtain:

$$0 = -\left(\overline{D_A}\frac{d\overline{C_A}}{dx} + \overline{D_B}\frac{d\overline{C_B}}{dx} - \overline{D_Y}\frac{d\overline{C_Y}}{dx}\right) + (\overline{C_A} + \overline{C_B} - \overline{C_Y})v_M$$

$$-\frac{F}{RT}\frac{d\overline{\psi}}{dx}(\overline{D_A}\,\overline{C_A} + \overline{D_B}\,\overline{C_B} + \overline{D_Y}\,\overline{C_Y})$$

so that

$$\frac{d\overline{\psi}}{dx} = \frac{RT}{F}\frac{v_M X + \left[(\overline{D_Y} - \overline{D_A})\dfrac{d\overline{C_A}}{dx} + (\overline{D_Y} - \overline{D_B})\dfrac{d\overline{C_B}}{dx}\right]}{[(\overline{D_Y} + \overline{D_A})\overline{C_A} + (\overline{D_Y} + \overline{D_B})\overline{C_B} - \overline{D_Y} X]} \quad (8)$$

For the counter ion A^+, the pseudo-thermodynamic equation becomes:

$$-\frac{\overline{J_A}}{\overline{D_A}}$$

$$= \frac{d\overline{C_A}}{dx} + \overline{C_A}\frac{v_M X + \left[(\overline{D_Y} - \overline{D_A})\dfrac{d\overline{C_A}}{dx} + (\overline{D_Y} - \overline{D_B})\dfrac{d\overline{C_B}}{dx}\right]}{[(\overline{D_Y} + \overline{D_A})\overline{C_A} + (\overline{D_Y} + \overline{D_B})\overline{C_B} - \overline{D_Y} X]}$$

$$-\frac{\overline{C_A}}{\overline{D_A}}v_M \quad (9)$$

which gives after rearrangement:

$$-\frac{\overline{J_A}}{\overline{D_A}}[(\overline{D_Y} + \overline{D_A})\overline{C_A} + (\overline{D_Y} + \overline{D_B})\overline{C_B} - \overline{D_Y} X]$$

$$+\frac{\overline{C_A}}{\overline{D_A}}v_M[(\overline{D_Y} + \overline{D_A})(\overline{C_A} - X) + (\overline{D_Y} + \overline{D_B})\overline{C_B}]$$

$$= [(2\overline{C_B} + \overline{C_B} - X)\overline{D_Y} + \overline{C_B}\,\overline{D_B}]\frac{d\overline{C_A}}{dx} + \overline{C_A}(\overline{D_Y} - \overline{D_B})\frac{d\overline{C_B}}{dx} \quad (10)$$

To obtain a similar equation for the counter ion B^+, we permute A and B in eqn. (10).

The application of the simplified pseudo-thermodynamic equation within a cation exchange-membrane, used in a bi-ionic system, leads to two coupled differential equations:

$$\overline{\alpha_{A0}} = \overline{\alpha_{A1}}\frac{d\overline{C_A}}{dx} + \overline{\alpha_{A2}}\frac{d\overline{C_B}}{dx} \quad (11a)$$

$$\overline{\alpha_{B0}} = \overline{\alpha_{B1}}\frac{d\overline{C_A}}{dx} + \overline{\alpha_{B2}}\frac{d\overline{C_B}}{dx} \quad (11b)$$

where the coefficients $\overline{\alpha_{ij}}$ depend on the A^+ and B^+ concentrations.

This differential equation system is written for the membrane phase. For each DBL phase, we have a similar system except we take $X = 0$:

$$\alpha_{A0} = \alpha_{A1}\frac{dC_A}{dx} + \alpha_{A2}\frac{dC_B}{dx} \quad (12a)$$

$$\alpha_{B0} = \alpha_{B1}\frac{dC_A}{dx} + \alpha_{B2}\frac{dC_B}{dx} \quad (12b)$$

where:

$$\alpha_{A0} = -\frac{J_A}{D_A}[(D_Y + D_A)C_A + (D_Y + D_B)C_B]$$

$$+\frac{C_A}{D_A}v_M[(D_Y + D_A)C_A + (D_Y + D_B)C_B]$$

$$\alpha_{A1} = (2C_A + C_B)D_Y + C_B D_B$$

$$\alpha_{A2} = C_A(D_Y - D_B)$$

$$\alpha_{B0} = -\frac{J_B}{D_B}[(D_Y + D_B)C_B + (D_Y + D_A)C_A]$$

$$+\frac{C_B}{D_B}v_M[(D_Y + D_B)C_B + (D_Y + D_A)C_A]$$

$$\alpha_{B1} = C_B(D_Y - D_A)$$

$$\alpha_{B2} = (2C_B + C_A)D_Y + C_A D_A$$

The integration of the coupled differential equation systems is only possible within an homogeneous and continuous phase, such as the membrane or a part of this membrane supposed homogeneous and the solutions constituting the DBL. In a bi-ionic system, we have shown each chemical species diffuses successively through three phases: DBL/IEM/DBL. At each interface, the concentrations are linked by the Donnan relation.

At the interface $x = 0$ (DBLa/IEM), it is easy to show that:

$$\frac{\overline{C_A(0)}}{C_A(0)} = \frac{\overline{C_B(0)}}{C_B(0)} = \frac{\overline{C_Y(0)}}{C_Y(0)} \quad (13)$$

or:

$$\frac{\overline{C_A(0)}}{C_A(0)} = \frac{\overline{C_B(0)}}{C_B(0)} = \frac{X + \overline{C_Y(0)} - \overline{C_A(0)}}{C_Y(0) - C_A(0)}$$

so that $\overline{C_A(0)}C_Y(0) = C_A(0)X + C_A(0)\overline{C_Y(0)}$. After reorganizing, we obtain the second-order polynomial:

$$\left(\frac{\overline{C_A(0)}}{C_A(0)}\right)^2 = \frac{X}{C_A(0) + C_B(0)}\frac{\overline{C_A(0)}}{C_A(0)} + 1$$

The positive solution of this polynomial is:

$$\frac{\overline{C_A(0)}}{C_A(0)} = \frac{X}{2[C_A(0) + C_B(0)]} + \sqrt{\left(\frac{X}{2[C_A(0) + C_B(0)]}\right)^2 + 1} \quad (14)$$

Now, we are able to solve numerically the set of equations obtained in the case of a bi-ionic potential where the water flow is considered. For this, we have developed a program[10] to evaluate theoretically the convection velocity contribution in the bi-ionic potential.

Results and Discussion

In a previous paper[3] we have determined the diffusion coefficients, $\overline{D_A}$, of K^+, Li^+ and Cl^- in the CM2 membrane and the diffusion boundary layer thickness, δ, for the two hydrodynamical conditions ($\omega = 0$ rpm or $\omega = 900$ rpm) in the absence of water flux. We have found that $\overline{D_{K^+}} = 3 \times 10^{-6}$ cm^2 s^{-1}, $\overline{D_{Li^+}} = 0.76 \times 10^{-6}$ cm^2 s^{-1} and $\overline{D_{Cl^-}} = 0.99 \times 10^{-6}$ cm^2 s^{-1} and that $\delta = 20$–23 μm without stirring or 3–4 μm for $\omega = 900$ rpm. The membrane was considered as homogeneous and the concentration of the functional sites, X, was computed from a classical method.[3]

We suppose that all the parameters (X, D_i, $\overline{D_i}$ and δ) remain constant even if the water flow is not negligible. This assumption is valid only in the case of a small water flow contribution to the bi-ionic potential values. If not, we must take into account this contribution to determine the three ion diffusion coefficients in the membrane and the diffusion boundary layer thickness.

Table 1 Water flow contribution to the bi-ionic potential values

	C_0/M	0.1	0.25	0.5	1.0	2.0	4.0
	$v_M/10^{-6}$ cm s^{-1}	−0.2	−0.36	−1.2	−0.8	+0.7	+3.7
$\omega = 0$	BIP(0)/mV	25.609	29.386	30.120	28.383	25.476	23.382
rpm	BIP(v_M)/mV	25.470	29.14	29.356	28.018	25.685	27.346
	ΔBIP/mV	−0.139	−0.246	−0.764	−0.365	+0.209	+3.964
	$v_M/10^{-6}$ cm s^{-1}	−0.3	−0.8	−1.2	−1.0	+0.7	+4.0
$\omega = 900$	BIP(0)/mV	32.524	33.517	32.692	30.010	26.599	24.059
rpm	BIP(v_M)/mV	32.312	32.800	31.942	30.474	26.811	24.766
	ΔBIP/mV	−0.212	−0.551	−0.750	+0.464	+0.212	+0.707

The BIP *vs.* v_M plots for the system KCl/CM2/LiCl are shown in Fig. 2(*a*) and 2(*b*) for the stirring rates $\omega_0 = 0$ rpm and $\omega_{max} = 900$ rpm, respectively, and for different common concentrations C_0. All the curves show that BIP varies linearly with v_M. The slope depends essentially on C_0 but not on ω. For a given value of ω, the slope is almost constant for low concentrations ($C_0 \leqslant 10^{-1}$ M) and decreases sharply for higher concentrations. This linear relationship between BIP and v_M justifies the assumption made at the end of the analytical resolution section, according to which the integrals $I_a^b(X)$ are constant and independent of the convection velocity.

In Table 1, we report, for each stirring rate ω, the measured convection velocity v_M,[4] the BIP values when $v_M = 0$ [BIP($v_M = 0$)], the BIP values for the experimental v_M [BIP(v_M)] and the difference ΔBIP = BIP(v_M) − BIP($v_M = 0$). We remark that ΔBIP has the same sign and the same variation with C_0 as v_M. In fact, ΔBIP increases with C_0, passes by a maximum and then decreases sharply. The maximum value of ΔBIP is estimated at 0.8 mV for the homogeneous membrane model. This value is smaller than the bi-ionic potential ones ($\approx 6\%$) but cannot be neglected because it represents more than five times the accuracy of the BIP measurements.[10]

On the other hand, we have shown theoretically that ΔBIP depends sharply on the ion diffusion coefficients in the membrane. In fact, the smaller the ion diffusion coefficients the greater the ΔBIP value. The proposed method can be useful in the case of interdiffusion through an ion-exchange membrane having smaller ion diffusion coefficients. We are working on determining these parameters for other membranes from their electric conductivities. The selectivity and the affinity coefficients will be measured and their influence on the interdiffusion process will be evaluated in a future paper.
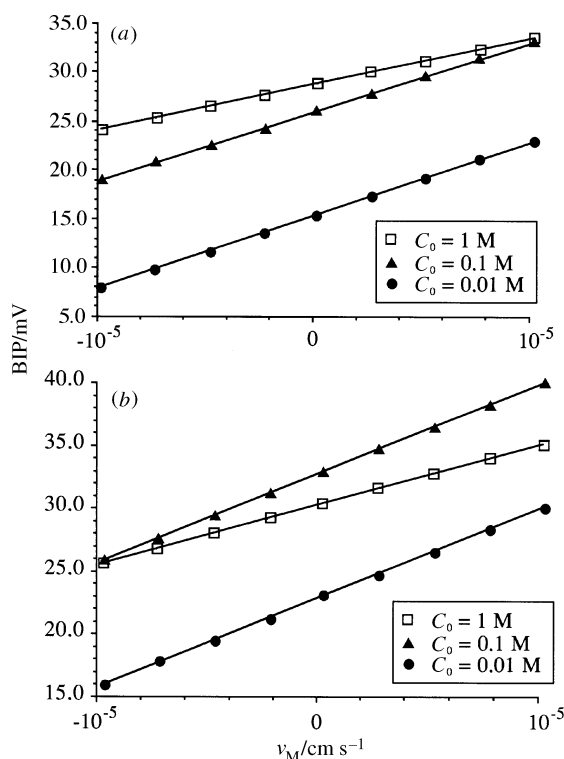
Conclusion

The measurement of the convection velocity, v_M, in the case of a bi-ionic system and the elaboration of a theoretical treatment based on a numerical resolution of the pseudo-thermodynamic equation, allowed us to evaluate the contribution of v_M to the bi-ionic potential. This contribution is of the order of 6%, which seems to be non-negligible. So, to take on a rigorous study of the interdiffusion process in a bi-ionic system, the convection velocity must be evaluated and its influence integrated. If not, all of the membrane and interdiffusion process characteristics, deduced from the bi-ionic potential data, remain approximate.

Fig. 2 BIP *vs.* the convection velocity, v_M, and the common concentration, C_0, for the bi-ionic system KCl/CM2/LiCl when (*a*) $\omega = 0$ rpm and (*b*) $\omega = 900$ rpm

References

1 K. Inenga and N. Yoshida, *J. Membr. Sci.*, 1980, **6**, 271.
2 A. Guirao, S. Mafé, J. A. Manzanares and J. A. Ibanèz, *J. Phys. Chem.*, 1995, **99**, 3387.
3 L. Dammak, C. Larchet, J. A. Manzanares, S. Mafé and B. Auclair, *J. Membr. Sci.*, 1996, **81**, 119.
4 L. Dammak, V. Tourreuil, C. Larchet and B. Auclair, *New J. Chem.*, 1997, **21**, 1291.
5 F. Helfferich, *Ions Exchange*, McGraw-Hill, New York, 1962.
6 Y. Toyoshima, Y. Kobatake and H. Fujita, *Trans. Faraday Soc.*, 1967, **63**, 2828.
7 R. Schlögl, *Ber. Bunsenges. Phys. Chem.*, 1966, **70**, 411.
8 D. Mackey and P. Meares, *Kolloidn. Zh.*, 1960, **171**, 139.
9 D. Mackey and P. Meares, *Kolloidn. Zh.*, 1959, **167**, 31.
10 L. Dammak, C. Larchet, J. A. Manzanares, V. V. Nikonenko and V. I. Zabolotsky, *Eur. Polym. J.*, 1996, **32**, 1199.