

# Equilibrium and transport properties of polydisperse polyelectrolytes in graft-modified porous charged membranes: forced permeation–diffusion of lignosulfonate

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The convective diffusion of a polydisperse polyelectrolyte (lignosulfonate) through charged porous membranes is studied. The membranes are characterised by potentiometric transport number determination both in the presence and in the absence of lignosulfonate. The convective diffusion experiments are carried out with NaCl and HCl as supporting electrolytes. The effect of using different concentrations of supporting electrolyte in the two cell compartments is also studied. The Donnan equilibrium and steady-state transport of the polyelectrolyte in a convective diffusion cell are theoretically described, and the effects of changing the supporting electrolyte (and pH) are discussed. Good agreement between theoretical and experimental results is obtained. It is shown that the effective membrane fixed charge reverses its sign due to polyelectrolyte adsorption.

## Introduction

The charge and conformation of polyelectrolytes are greatly dependent on their environment, *i.e.* solvent, ionic strength, temperature, electric fields, *etc.*<sup>1,2</sup> Polyelectrolytes, and especially proteins, are often characterised by using electrophoresis.<sup>3</sup> However, the analysis of experimental data in terms of the electrophoretic mobility and the charge number presents a theoretical problem which has not yet been solved in a satisfactory manner. This is due to the simplifications which have usually been made in the theory, *e.g.* the perturbing influence of the external electric field on the ionic distribution in the electrical double layer is neglected. In previous work, we described a method to determine the ionic diffusion coefficients and effective charge numbers of a polyelectrolyte which avoided these difficulties.<sup>4,5</sup> The method employs the convective diffusion process in a non-charged porous membrane and the data obtained is analysed within the theoretical framework of extended Nernst–Planck equations.<sup>6,7</sup>

A model substance of high practical interest showing typical polyelectrolyte behavior is lignosulfonate.<sup>8</sup> The lignin is a branched macromolecule binding the wood cells together. In the pulping process the covalent linkages between the lignin and the carbohydrates present are split and the lignin is broken down to fragments of varying molecular masses (polydispersity). This is achieved by digestion with solutions of sulfuric acid and its salts, which results in sulfonation at the benzylic carbon atoms of the molecule. Thus, lignosulfonate molecules contain sulfonate groups and phenolic hydroxy groups. The molar masses of this polydisperse polyelectrolyte can vary from  $10^3$  to  $10^6$  g mol<sup>-1</sup>. The most important characteristic of lignosulfonates is that their molecular shape in solution depends on the net electrical charge on the molecule. In the uncharged state the molecule curls up. In the charged state the molecule extends in spherical form. Thus it is

obvious that the ionic diffusion coefficients of lignosulfonates depend on pH.<sup>9</sup>

In order to characterise the transport behaviour of this polydisperse polyelectrolyte, diffusion coefficients and effective charge numbers of lignosulfonates were studied by the above mentioned convective diffusion method as a function of the pH,<sup>4,5</sup> the ionic strength,<sup>10</sup> the temperature,<sup>11,12</sup> the relative permittivity<sup>13</sup> and the applied electric field.<sup>14</sup> All this previous work was restricted to non-charged porous membranes because of the high mechanical permeability required by the method. Modern membrane preparation procedures, such as radiation<sup>15</sup> or plasma induced<sup>16</sup> graft copolymerization, have made available charged porous membranes which combine satisfactorily permselectivity and mechanical permeability. In particular, the grafting method is very interesting because it allows control of the membrane properties through the degree of grafting.<sup>17</sup> Furthermore, the permeability of the grafted membranes is sensitive to the environment and can be modified by changes in temperature,<sup>18</sup> pH,<sup>19,20</sup> and salt concentration<sup>21</sup> as well as by applying an external electric field.<sup>22,23</sup> The aim of this work is to study the convective diffusion of polyelectrolytes through charged porous membranes. Experimental results are obtained when the cell compartments contain NaCl and HCl as supporting electrolytes. The Donnan equilibrium and steady-state transport of lignosulfonates in a convective diffusion cell are theoretically described, and the effects of changing the supporting electrolyte on lignosulfonate transport are discussed.

The study of lignosulfonate transport through graft-modified porous charged membranes poses some problems which are also relevant to other related fields. First, some biophysical problems involve the equilibrium distribution of polyvalent macroions in a charged membrane.<sup>24</sup> The classical Donnan equilibrium model has to be extended to describe the partition between the membrane and the external solutions of

the different polyelectrolyte fractions. Second, the efficiency of the supporting electrolyte introduced to prevent migration is critically analysed. The criteria established for the validity of the negligible migrational transport assumption developed here can be applied to similar electrochemical problems.

## Experimental

### Apparatus

The experimental apparatus is shown schematically in Fig. 1. The cell is divided into two compartments  $\alpha$  and  $\beta$  separated by a charged porous membrane. The feed solution pumped into the  $\alpha$  compartment at constant rate  $\dot{V}^0$  contains supporting electrolyte (NaCl or HCl) at a concentration  $c^0$ . The feed solution pumped into the  $\beta$  compartment at constant rate  $\dot{V}^s$  contains supporting electrolyte at a concentration  $c^s$  and the polyelectrolyte at a concentration  $c_{LS}^s$ . The solution in  $\alpha$  compartment is pumped out at a constant rate  $\dot{V}^\alpha$  while  $\dot{V}^\beta$  is a free outlet flow. The convective flow  $\dot{V}^c$  is then the difference  $\dot{V}^0 - \dot{V}^\alpha$ . Both compartments are stirred with the aid of magnetic fleas. The cell used is described in detail in ref. 25.

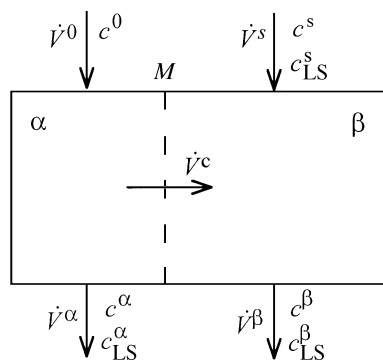
### Materials and analysis

The sodium chloride, potassium chloride and hydrochloric acid used were *pro analysis* grade. The sodium lignosulfonate was purified at Borregaard, Norway. It contained *ca.* 99% lignosulfonate and 1% carbohydrates. The molar mass distribution of lignosulfonate and the concentration ratio were determined by gel chromatography as described earlier.<sup>4</sup> Sodium concentrations were analysed by AAS.

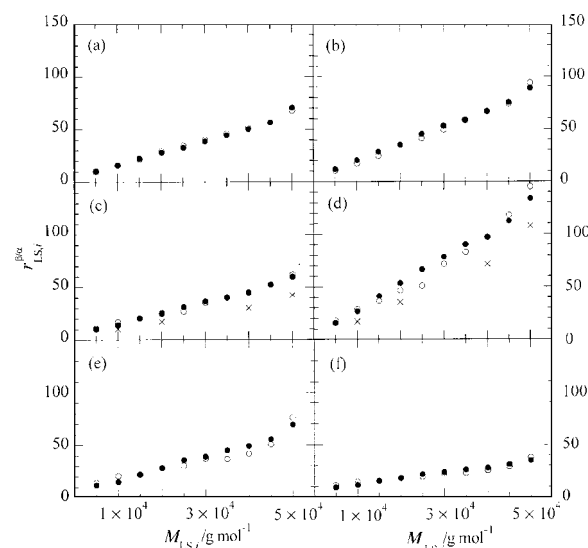
The anion-exchange membrane used (ref. code 2AM22) was a Millipore PVDF membrane (pore size 0.45  $\mu\text{m}$ ) grafted with trimethylamine. The degree of grafting was 22% reached by 2 h amination using the procedure described earlier.<sup>17</sup> The measured ion exchange capacity was 1  $\text{mmol g}^{-1}$  of dry membrane.

### Convective diffusion experiments

The polyelectrolyte is described as  $n = 10$  species of diffusion coefficients  $D_{LS,i}$ , effective charge numbers  $z_{LS,i}$  and molecular masses  $M_{LS,i} = 5000 \text{ g mol}^{-1}$ , with  $i = 1, \dots, n$  (*i.e.*,  $M_{LS,i}$  varies from 5000 to 50 000  $\text{g mol}^{-1}$ ). The experimental results are presented in the form of the concentration ratio  $r_{LS,i}^{\beta/\alpha} = c_{LS,i}^\beta / c_{LS,i}^\alpha$  determined by gel chromatography. The lignosulfonate species are introduced in the  $\beta$  compartment with a homogeneous distribution (in molar concentration), so that all lignosulfonate species have the same molar concentration,  $c_{LS,i}^\beta = c_{LS}^\beta / n$ . These species diffuse through the membrane against the convective flow towards the  $\alpha$  compartment (see Fig. 1).



**Fig. 1** Schematic drawing of the cell.  $M$  is the charged porous membrane of surface area  $A$  and thickness  $l$ . The flow rates are indicated. The supporting electrolyte is fed to both compartments. Lignosulfonate is fed to the  $\beta$  compartment only.



**Fig. 2** Concentration ratio  $r_{LS,i}^{\beta/\alpha}$  of the lignosulfonate species in the experiments: (a) 0.01 M NaCl with  $c^0 \approx c^s$ , (b) 0.01 M NaCl with  $3c^0 \approx c^s$ , (c) 0.1 M NaCl with  $c^0 \approx c^s$ , (d) 0.1 M NaCl with  $3c^0 \approx c^s$ , (e) 0.1 M HCl with  $c^0 \approx c^s$ , and (f) 0.1 M HCl with  $3c^0 \approx c^s$ . (See Table 1 for the exact concentration values.) Full symbols are the experimental data, and open symbols are the theoretical results obtained with the transport model described in next section. The crosses ( $\times$ ) correspond to experimental data from ref. 26 corresponding to a neutral porous membrane under similar experimental conditions.

Fig. 2 shows the results obtained when *ca.*  $2 \text{ g l}^{-1}$  of lignosulfonate was fed to the  $\beta$  compartment. Experiments (a)–(d) correspond to NaCl as supporting electrolyte. Experiments (e) and (f) correspond to HCl as supporting electrolyte. Experiments (a), (c) and (e) have been carried out using approximately the same concentration of supporting electrolyte in the two compartments, 10, 100 and 100 mM, respectively. Experiments (b), (d) and (f) have been conducted feeding the supporting electrolyte in  $\beta$  compartment at a concentration about three times larger than in  $\alpha$  compartment,  $3c^0 \approx c^s$ . The actual concentration and volume flow rates are shown in Table 1. The convective flow  $\dot{V}^c$  is determined as the difference  $\dot{V}^0 - \dot{V}^\alpha$ .

A number of observations can be drawn from Fig. 2. First, the increase in the concentration ratio  $r_{LS,i}^{\beta/\alpha}$  with the molar mass of the lignosulfonate is very similar to that observed in previous studies with non-charged porous membranes.<sup>5,13,14,26</sup> Second, the supporting electrolyte concentration difference between the two compartments has a different effect for NaCl and HCl. When NaCl is used,  $r_{LS,i}^{\beta/\alpha}$  is larger in the cases  $3c^0 \approx c^s$  [Fig. 2(b) and 2(d)] than in the cases  $c^0 \approx c^s$  [Fig. 2(a) and 2(c)]. The opposite is true when HCl is used as supporting electrolyte [Fig. 2(e) and 2(f)]. Third,  $r_{LS,i}^{\beta/\alpha}$  apparently increases with the supporting electrolyte concentration. This effect is clearly seen from the comparison of Fig. 2(b) and 2(d). The reason why it is not observed in Fig. 2(a) and 2(c) could be the accidental difference between  $c^\alpha$  and  $c^\beta$  in experiment (a) (see Table 1), which leads to higher values of the ratio  $r_{LS,i}^{\beta/\alpha}$  as already commented. Fourth and last, although the lignosulfonate effective charge numbers are much smaller when HCl is used as supporting electrolyte (see Table 2), there is no significant difference in the measured values of the ratio  $r_{LS,i}^{\beta/\alpha}$  [compare Fig. 2(c) and 2(e)].

### Transport number measurements

In order to have an estimate of the fixed charge concentration of the membrane 2AM22, transport number measurements were carried out in a concentration cell with KCl bathing solutions using a methodology suitable for highly porous

**Table 1** Input and output flow rates and concentrations in the different experiments

	Experiment					
	(a)	(b)	(c)	(d)	(e)	(f)
$\dot{V}^0/\text{ml h}^{-1}$	0.479	0.482	0.563	0.561	0.562	0.562
$\dot{V}^s/\text{ml h}^{-1}$	0.469	0.473	0.564	0.566	0.565	0.567
$\dot{V}^\alpha/\text{ml h}^{-1}$	0.363	0.364	0.424	0.428	0.431	0.430
$\dot{V}^\beta/\text{ml h}^{-1}$	0.566	0.571	0.679	0.679	0.674	0.681
$c^0/\text{mol l}^{-1}$	0.0098	0.0052	0.097	0.050	0.102	0.052
$c^s/\text{mol l}^{-1}$	0.0133	0.0174	0.101	0.146	0.103	0.148
$c^\alpha/\text{mol l}^{-1}$	0.0110	0.0097	0.103	0.085	0.103	0.093
$c^\beta/\text{mol l}^{-1}$	0.0127	0.0135	0.102	0.108	0.103	0.107
$c_{\text{LS}}^s/\text{g l}^{-1}$	1.943	1.953	1.992	1.975	1.910	1.926

membranes.<sup>27</sup> The co-ion transport numbers  $\bar{t}_{\text{K}^+}$  were 0.055 for concentrations  $c^\beta = 2c^\alpha = 20$  mM, and 0.27 for concentrations  $c^\beta = 2c^\alpha = 200$  mM. As expected, the membrane behaves as an anion-exchange membrane and the fixed charge concentration can be estimated to be of the order of 100 mM from the transport numbers observed and the Donnan equilibrium equations. Since this value is of the order of the electrolyte concentrations, large Donnan potential drops occur at the membrane/solution interfaces and the co-ion exclusion is very good.

There are, however, important differences between these transport number measurements and the convective diffusion experiments reported above regarding the Donnan phenomena. It is well known that the co-ion exclusion is poorer in the presence of multivalent counterions because the charged membrane prefers multivalent to monovalent counterions and this decreases the absolute value of the Donnan potential.<sup>28</sup> Therefore, the presence of even small amounts of highly charged lignosulfonate molecules is expected to reduce the Donnan potential drops. The poor co-ion exclusion and the large polyelectrolyte uptake would result in high values of both the co-ion and the lignosulfonate transport numbers within the membrane. To check experimentally this effect, further transport number measurements were carried out in the presence of lignosulfonate. In particular,  $1 \text{ g l}^{-1}$  of lignosulfonate was added to the KCl solutions and the observed co-ion transport numbers  $\bar{t}_{\text{K}^+}$  were 0.38 for concentrations  $c^\beta = 2c^\alpha = 20$  mM, and 0.37 for concentrations  $c^\beta = 2c^\alpha = 200$  mM. Since  $t_{\text{K}^+}$  takes the value 0.49 in (an infinitely dilute) bulk solution, we conclude that the membrane still behaves as anion-exchange membrane. Moreover, the fact that  $\bar{t}_{\text{K}^+}$  attains practically the same value in both determinations implies that the Donnan potential is mostly controlled by the lignosulfonate and not by the supporting electrolyte.

## Theory

### System description

The membrane is modelled as a homogeneous phase with a uniform molar concentration  $c_m$  of fixed groups of charge number  $z_m$ . The membrane thickness and the effective membrane area are denoted by  $l$  and  $A$ , respectively. The effect of the diffusion boundary layers flanking the membrane is neglected. The transport problem is assumed to be one-dimensional with the position coordinate  $x$  varying from  $x = 0$  ( $\alpha$  compartment) to  $x = l$  ( $\beta$  compartment).

Owing to the high membrane porosity and water content, no chemical partition coefficients are included in the modelling, and the same values for the diffusion coefficients are used inside and outside the membrane. Furthermore, the electrolyte solutions are considered to be ideal; *i.e.* activity coefficients are set equal to unity.

### Balance equations

Under steady-state conditions, the mass conservation principle implies that (see Fig. 1)

$$J_i = c_i^0 \dot{V}^0 - c_i^\alpha \dot{V}^\alpha = c_i^\beta \dot{V}^\beta - c_i^s \dot{V}^s \quad (1)$$

where  $J_i$  is the flux of species  $i$  through the membrane. Eqn. (1) constitutes a relation between the concentration of species  $i$  in  $\alpha$  and  $\beta$  compartments, which is very important in the case of lignosulfonate species because it is the concentration ratio  $r_{\text{LS},i}^{\beta/\alpha} = c_{\text{LS},i}^\beta / c_{\text{LS},i}^\alpha$  rather than the individual concentrations that is measured by gel chromatography. The concentrations  $c_{\text{LS},i}^\alpha$  and  $c_{\text{LS},i}^\beta$  are then obtained as

$$c_{\text{LS},i}^\alpha = \frac{c_{\text{LS},i}^s \dot{V}^s}{\dot{V}^\alpha + r_{\text{LS},i}^{\beta/\alpha} \dot{V}^\beta}, \quad i = 1, \dots, n \quad (2a)$$

$$c_{\text{LS},i}^\beta = r_{\text{LS},i}^{\beta/\alpha} c_{\text{LS},i}^\alpha, \quad i = 1, \dots, n \quad (2b)$$

where the experimental condition  $c_{\text{LS},i}^0 = 0$  has been used. Furthermore, eqn. (1) shows that the fluxes of the lignosulfonate species are given by

$$J_{\text{LS},i} = -c_{\text{LS},i}^\alpha \dot{V}^\alpha, \quad i = 1, \dots, n \quad (3)$$

where the minus sign means that the transport takes place from  $\beta$  to  $\alpha$  compartment, and hence against the convective flow.

Eqn. (3) clearly shows that the flux of a given lignosulfonate species is proportional to its concentration in  $\alpha$  compartment, so that a large value of the ratio  $r_{\text{LS},i}^{\beta/\alpha}$  implies a low flux of species LS,  $i$ . Furthermore, since the flux direction is determined by the diffusion process, the ratio  $r_{\text{LS},i}^{\beta/\alpha}$  will be larger for those species having the lower diffusional coefficient, which turn out to be the larger molar mass fractions.

### Donnan equilibrium

The partition of a charged species  $i$  between the membrane phase and the bathing solution is determined by the equality of its electrochemical potential in the two phases, which can be expressed as

$$\bar{c}_i = c_i e^{-z_i f \Delta \phi_D} \quad (4)$$

where  $c_i$  is the molar concentration at the membrane/solution interface,  $f = F/RT$  where  $F$  the Faraday constant,  $R$  the gas constant and  $T$  the absolute temperature, and  $\Delta \phi_D = \bar{\phi} - \phi$  is the Donnan potential. Overbars are used to denote magnitudes in membrane phase.

The Donnan potential is determined from the condition that both phases must be locally electroneutral

$$c_+ - c_- + \sum_{\text{LS},i} z_{\text{LS},i} c_{\text{LS},i} = 0 \quad (5)$$

and

$$\bar{c}_+ - \bar{c}_- + \sum_{\text{LS},i} z_{\text{LS},i} \bar{c}_{\text{LS},i} + z_m c_m = 0 \quad (6)$$

where the first terms correspond to the supporting electrolyte ions. Combining eqns. (4) and (6) yields

$$c_+ e^{-f\Delta\phi_D} - c_- e^{f\Delta\phi_D} + \sum_{LS,i} z_{LS,i} c_{LS,i} e^{-z_{LS,i} f\Delta\phi_D} + z_m c_m = 0 \quad (7)$$

which can be used together with eqn. (5) to eliminate the supporting electrolyte cation concentration and obtain an algebraic equation in the variable  $E = e^{f\Delta\phi_D}$ ,

$$-c_-(E^2 - 1) + \sum_{LS,i} z_{LS,i} c_{LS,i} (E^{1-z_{LS,i}} - 1) + z_m c_m E = 0 \quad (8)$$

that can be solved by numerical methods.

### Transport equations

Under steady-state conditions, the extended Nernst-Planck equations for the ion flux of species  $i$

$$J_i = -AD_i \left( \frac{d\bar{c}_i}{dx} + z_i \bar{c}_i f \frac{d\bar{\phi}}{dx} \right) + \bar{c}_i \dot{V}^c \quad (9)$$

can be interpreted as a linear first-order differential equation in  $\bar{c}_i$ . By using  $\exp(z_i f \bar{\phi} - \dot{V}^c x / AD_i)$  as integrating factor, eqn. (9) can be formally integrated over the membrane thickness to give

$$J_i = -AD_i \frac{\bar{c}_i(l) e^{z_i f \bar{\Delta}\bar{\phi}} e^{-\dot{V}^c l / AD_i} - \bar{c}_i(0)}{\int_0^l e^{z_i f [\bar{\phi} - \bar{\phi}(0)]} e^{-\dot{V}^c x / AD_i} dx} \quad (10)$$

where  $\bar{\Delta}\bar{\phi} = \bar{\phi}(l) - \bar{\phi}(0)$  is the potential drop within the membrane. Owing to the presence of supporting electrolyte, this potential drop might be expected to be negligible, which would reduce eqn. (10) to the simpler form

$$J_i = \dot{V}^c \frac{\bar{c}_i(l) e^{-\dot{V}^c l / AD_i} - \bar{c}_i(0)}{e^{-\dot{V}^c l / AD_i} - 1} \quad (11)$$

However, this procedure requires a more thorough analysis. The electric potential drop within the membrane has three contributions, namely, the diffusion potential drop, the streaming potential drop and the ohmic drop. In the absence of electric current, only the first two terms are relevant. The streaming potential drop is inversely proportional to the electrolyte concentration inside the membrane, so that it is reduced by the addition of supporting electrolyte. The diffusion potential drop is related to the different mobilities of the ionic species and the concentration differences between the two membrane boundaries. Thus, the supporting electrolyte reduces the diffusion potential drop only when it is added at the same concentration in the two compartments. Therefore, we cannot assume the absence of potential drop within the membrane simply because of the addition of supporting electrolyte.

The relevance of the potential drop  $\bar{\Delta}\bar{\phi}$  must be analysed in relation to its influence on the transport of the lignosulfonate species. A frequently used approximation that allows us to evaluate the integral in eqn. (10) is the Goldman constant field assumption.<sup>29</sup> In this case, the ion fluxes are approximately given by

$$J_i = \dot{V}_{\text{eff}}^c \frac{\bar{c}_i(l) e^{-\dot{V}_{\text{eff}}^c l / AD_i} - \bar{c}_i(0)}{e^{-\dot{V}_{\text{eff}}^c l / AD_i} - 1} \quad (12)$$

where

$$\dot{V}_{\text{eff}}^c = \dot{V}^c - z_i AD_i f \frac{\Delta\bar{\phi}}{l} \quad (13)$$

The potential drop  $\bar{\Delta}\bar{\phi}$  will be important in those cases where the second term in eqn. (13) is of the same order as the first

term, that is,  $\bar{\Delta}\bar{\phi} \approx \dot{V}^c l / z_i AD_i f$ . Taking  $\dot{V}^c \approx 3 \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$ ,  $A/l \approx 20 \text{ cm}$ ,  $z_i \approx 10$  and  $D_i \approx 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  as typical values, we conclude that a potential drop as small as 4 mV will have the same influence on the lignosulfonate transport as the convective flow. Yet, the local migrational transport numbers of the lignosulfonates species are several orders of magnitude smaller than those of the supporting electrolyte species.

Eqns. (10)–(12) involve the so-called membrane constant  $A/l$  (effective membrane area/membrane thickness). This is a key parameter in convective diffusion processes which has to be determined either by fitting the experimental data or from a separate measurement.<sup>30</sup> In the case of neutral membranes ( $c_m = 0$ ) the membrane constant can be determined by adding a small amount of a trace ion (*e.g.* potassium ion) to the feed solution for compartment  $\beta$  ( $c_{\text{trace}}^0 = 0$ ,  $c_{\text{trace}}^s \neq 0$ ). Since the migrational term can be neglected in the flux equation for this ion,<sup>31</sup> eqns. (1) and (11) could be used to determine the membrane constant as

$$\frac{A}{l} = \frac{\dot{V}^c}{D_{\text{trace}}} \left\{ \ln \left[ \left( \frac{c_{\text{trace}}^\beta}{c_{\text{trace}}^\alpha} + \frac{\dot{V}^\alpha}{\dot{V}^c} \right) \left( 1 + \frac{\dot{V}^\alpha}{\dot{V}^c} \right) \right] \right\}^{-1} \quad (14a)$$

In the case of charged membranes, eqn. (4) has to be taken into account and the following equation is obtained

$$\frac{A}{l} = \frac{\dot{V}^c}{D_{\text{trace}}} \left\{ \ln \left[ \left( \frac{c_{\text{trace}}^\beta}{c_{\text{trace}}^\alpha} e^{-f\Delta\phi_B} + \frac{\dot{V}^\alpha}{\dot{V}_{\text{eff}}^c} \right) \left( e^{-f\Delta\phi_B} + \frac{\dot{V}^\alpha}{\dot{V}_{\text{eff}}^c} \right) \right] \right\}^{-1} \quad (14b)$$

However, eqn. (14b) is not so useful because it contains two unknown membrane parameters,  $A/l$  and  $c_m$ , which cannot be determined from a single concentration ratio measurement,  $c_{\text{trace}}^\beta / c_{\text{trace}}^\alpha$ . In conclusion, though eqn. (14a) constitutes the basis for the procedure we have followed in our previous studies, eqn. (14b) will not be used in the present work.

### Determination of the diffusion potential drop within the membrane

Since supporting electrolyte ions are present in a much higher concentration than the other charged species, their fluxes are much larger than those of any other species. Thus, the zero electric current condition can be written as  $J_+ \approx J_- = J$ , where  $J$  is the salt flux, and the potential drop within the membrane  $\bar{\Delta}\bar{\phi}$  can be estimated from the integration of eqn. (9) for  $i = +, -$  by using the local electroneutrality assumption

$$\bar{c}_+ - \bar{c}_- + z_m c_m \approx 0 \quad (15)$$

The ion concentrations at  $x = 0$  and  $l$  are used as boundary conditions, since they are known from the measured concentrations in the two compartments and eqn. (4).

As a preliminary step in the potential drop evaluation, the salt flux has to be determined. Eliminating the electric potential gradient from the two transport equations, and using eqn. (15) to relate the derivatives  $d\bar{c}_+/dx$  and  $d\bar{c}_-/dx$ , it is seen that

$$\frac{AD}{2\dot{V}^c} (\bar{c}_+ + \bar{c}_-) \frac{d\bar{c}_+}{dx} = \bar{c}_+ \bar{c}_- - (\bar{c}_+ t_+^b + \bar{c}_- t_-^b) \frac{J}{\dot{V}^c} \quad (16)$$

where  $t_i^b \equiv D_i / (D_+ + D_-)$  is the transport number of species  $i$  ( $i = +, -$ ) in bulk solution and  $D \equiv 2D_+ D_- / (D_+ + D_-)$  is the salt diffusion coefficient. After transforming variables to  $\bar{C} \equiv \bar{c}_+ + \bar{c}_-$  with the help of eqn. (15), eqn. (16) can be inte-

**Table 2** Diffusion coefficients and effective charge numbers of the lignosulfonate species from refs. 11, 14 and 15

$M_{LS,i}/g\ mol^{-1}$	Experiments (a), (b)		Experiments (c), (d)		Experiments (e), (f)	
	$D_{LS,i}/10^{-6}\ cm^2\ s^{-1}$	$z_{LS,i}$	$D_{LS,i}/10^{-6}\ cm^2\ s^{-1}$	$z_{LS,i}$	$D_{LS,i}/10^{-6}\ cm^2\ s^{-1}$	$z_{LS,i}$
5000	1.41	-6.2	1.58	-5.3	2.20	+0.2
10000	1.11	-8.5	1.31	-8.1	1.89	-0.6
15000	0.98	-10.8	1.16	-8.9	1.74	-1.0
20000	0.88	-12.8	1.09	-10.6	1.60	-1.9
25000	0.84	-14.5	1.05	-11.1	1.53	-2.1
30000	0.81	-16.2	0.97	-13.0	1.44	-2.7
35000	0.79	-17.9	0.94	-14.1	1.41	-2.3
40000	0.77	-19.2	0.91	-15.0	1.35	-2.5
45000	0.75	-20.1	0.87	-16.1	1.28	-3.1
50000	0.72	-22.2	0.84	-17.7	1.16	-4.7

grated by standard methods to give

$$\frac{1}{r_1 - r_2} \ln \left[ \left( \frac{\bar{C}(l) - r_1}{\bar{C}(0) - r_1} \right)^{r_1} \left( \frac{\bar{C}(0) - r_2}{\bar{C}(l) - r_2} \right)^{r_2} \right] = \frac{\dot{V}c_l}{AD} \quad (17)$$

where  $r_1$  and  $r_2$  are the roots of the following algebraic equation in  $\bar{C}$

$$\bar{C}^2 - 2[\bar{C} - z_m c_m (t_+^b - t_-^b)] \frac{J}{\dot{V}c} - z_m^2 c_m^2 = 0 \quad (18)$$

The expression of the electric potential drop is obtained by eliminating first the concentration gradients from eqn. (9) for  $i = +, -$

$$\frac{AD}{2\dot{V}c} (\bar{c}_+ + \bar{c}_-) f \frac{d\bar{\phi}}{dx} = \bar{c}_+ t_-^b - \bar{c}_- t_+^b + (t_+^b - t_-^b) \frac{J}{\dot{V}c} \quad (19)$$

and second the position variable from the transformed eqns. (16) and (19). It is then concluded that

$$f\bar{\Delta\phi} = -(t_+^b - t_-^b) \frac{\dot{V}c_l}{AD} + \frac{(r_1 + r_2)(t_+^b - t_-^b) - z_m c_m}{r_1 - r_2} \times \ln \left[ \frac{(\bar{C}(l) - r_1)(\bar{C}(0) - r_2)}{(\bar{C}(0) - r_1)(\bar{C}(l) - r_2)} \right] \quad (20)$$

where the salt flux  $J$ , and consequently  $r_1$  and  $r_2$ , are determined from eqn. (17). Note that eqn. (20) contains both the diffusion potential and the streaming potential contributions.

### Analysis of the convective diffusion experiments

The experimental results in Fig. 2 are analysed using infinite dilution values for the diffusion coefficients of sodium and chloride ions,<sup>32</sup> and the previously determined<sup>5,13,14</sup> diffusion coefficients and effective charge numbers of the lignosulfonate species shown in Table 2. These values deserve some comment before proceeding to the analysis of the convective diffusion experiments. First, it should be noted that increasing the supporting electrolyte concentration leads to a better screening of the electrostatic interactions between the polyelectrolyte charges so that the polyelectrolyte collapses<sup>33</sup> and its diffusion coefficient increases. This better screening of the polyelectrolyte charges implies a modification of the dissociation equilibria at the surface of the spherical polyelectrolyte so that the polyelectrolyte surface charge density increases. However, the polyelectrolyte collapse causes the effective charge numbers  $z_{LS,i}$  to decrease when the supporting electrolyte concentration is increased because the average distance between fixed charge groups decreases then. Second, decreasing the pH below the  $pK_a$  of the polyelectrolyte surface groups reduces significantly its effective charge number and the polyelectrolyte contracts again,<sup>33</sup> thus increasing its diffusion coefficient again. These are the trends observed in Table 2.

The concentrations of the lignosulfonate species in both compartments are determined from eqns. (2a) and (2b). The Donnan equilibria, eqn. (8), are then solved with an initial

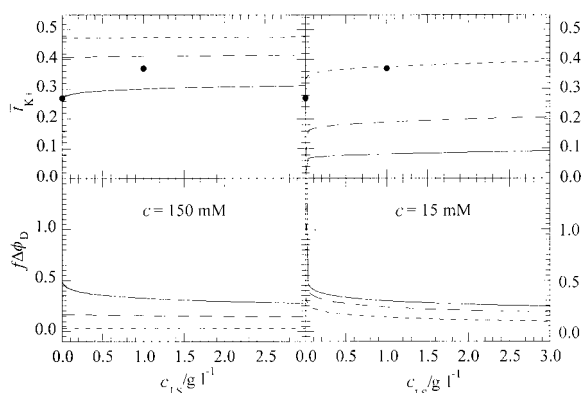
guess of the membrane fixed charge concentration  $z_m c_m$ . The potential drop within the membrane is then obtained from eqn. (20), also with an initial guess of the membrane constant  $A/l$ . The lignosulfonate concentration in the  $\alpha$  compartment  $c_{LS,i}^\alpha$  and the ratio  $r_{LS,i}^{\beta/\alpha}$  are then determined from eqns. (1) and (12). Finally, the procedure is iterated to improve the agreement between the observed and predicted values of the ratio  $r_{LS,i}^{\beta/\alpha}$ . The theoretical results are shown in Fig. 2 as open symbols. The agreement is remarkably good given the complexity of the system considered and the approximations made in the theoretical analysis.

During the iteration procedure,  $z_m c_m$  and  $A/l$  are used as fitting parameters. Table 3 summarises the values of these two parameters, as well as the potential drop  $\bar{\Delta\phi}$ . Surprisingly, the values of the effective membrane fixed charge concentration  $z_m c_m$  are negative despite the fact that the porous membranes had been grafted with trimethylamine and were expected to behave as anion-exchange membranes. A deeper analysis shows that the fact should not be so surprising. It has long been known that multivalent counterions can associate with the fixed charge groups in the membrane to such an extent that the effective membrane fixed charge may be reversed.<sup>28,34</sup> The effect is more pronounced in the case of polyelectrolytes, so that anion-exchange membranes may behave as cation-exchange membranes due to polyelectrolyte adsorption.<sup>35-37</sup> This charge overcompensation has been predicted theoretically and confirmed experimentally in several studies (see ref. 38 and references therein) and is related to short-range interactions of the polyelectrolyte with the grafted membrane.

It is worth mentioning that the fitting procedure employed here is very sensitive to the value of  $z_m c_m$ , so that the results in Table 3 can be considered as reliable determinations of the effective membrane fixed charge and, consequently, as an indirect proof of the polyelectrolyte adsorption phenomenon. In particular, Table 3 shows that the charge overcompensation is larger in experiments (c)–(f), which implies that the lignosulfonate adsorption increases with the electrolyte concentration. Once again, this is in agreement with other experimental observations, which predict that the polyelectrolyte adsorption is proportional to the square root of the ionic strength.<sup>39</sup> Note also that all values of the effective membrane fixed charge in Table 3 are much smaller than the supporting electrolyte concentration what indicates that the Donnan potential drops are small. Hence, the behaviour of the

**Table 3** Parameters obtained from the theoretical analysis of the convective diffusion experiments

	Experiment					
	(a)	(b)	(c)	(d)	(e)	(f)
$z_m c_m / \text{mM}$	-1.1	-0.3	-12.0	-7.0	-16.0	-16.0
$(A/l) / \text{cm}$	22	22	22	17	12	14
$f\bar{\Delta\phi}$	0.0338	0.0698	0.0036	0.0544	0.0039	-0.0815



**Fig. 3** Co-ion transport numbers  $\bar{t}_{K^+}$  and Donnan potential  $\Delta\phi_D$  (in units  $RT/F$ ) obtained from simulations of the state of a membrane in equilibrium with a solution containing KCl at concentration  $c = 150$  or  $15\text{ mM}$  and lignosulfonate at a total concentration  $c_{LS}$  of  $0$  to  $3.0\text{ g l}^{-1}$  with a homogenous molar distribution. The lines correspond to different values of the effective membrane fixed charge concentration,  $z_m c_m = 150\text{ mM}$  (—),  $50\text{ mM}$  (---), and  $10\text{ mM}$  (· · ·). The full symbols are the transport numbers determined potentiometrically. The diffusion coefficients and effective charge numbers of the lignosulfonate species have been taken from Table 2 (first columns for  $c = 15\text{ mM}$ , middle columns for  $c = 150\text{ mM}$ ).

lignosulfonate species is not so much influenced by their effective charge numbers, which explains the relatively small difference observed between experiments (c) and (e) in Fig. 2.

The variations observed in the membrane constant  $A/l$  from one experiment to another could also be due to the polyelectrolyte adsorption as well as to possible stretching of the membrane grafted chains. Nevertheless, this parameter is often affected by significant uncertainties.<sup>4,5</sup>

The potential drop values of Table 3 deserve some comment. When NaCl is used as supporting electrolyte, the potential drop  $\Delta\bar{\phi}$  is invariably positive. When HCl is used, the potential drop  $\Delta\bar{\phi}$  is either positive and small or negative. A difference must be made between the cases with no significant concentration difference [experiments (c) and (e)] and those where the concentration in  $\beta$  compartment was larger than in  $\alpha$  compartment [experiments (a), (b), (d) and (f); an accidental concentration difference existed in experiment (a)]. In the first cases, there is no diffusion potential and the observed potential drops are basically due to the streaming potential contribution. Since the effective membrane fixed charge is negative and the solvent flows from  $\alpha$  to  $\beta$  compartment, the streaming potential drop is positive (*i.e.*, the membrane end flanking the  $\beta$  side is positive with respect to the  $\alpha$  side). When  $c^\beta$  is significantly larger than  $c^\alpha$ , the dominant term is the diffusion potential. Since diffusion takes place from  $\beta$  to  $\alpha$  compartment and chloride ion is faster than sodium ion, the diffusion potential drop is positive in the case of NaCl. Conversely, since hydrogen ion moves faster than chloride ion, the diffusion potential drop is negative in the case of HCl. These are indeed the results obtained.

We are now in a position to explain why the supporting electrolyte concentration difference between the two compartments have a different effect on  $r_{LS,i}^{\beta/\alpha}$  for NaCl and HCl. When NaCl is used, the migrational contribution to the transport of lignosulfonate species is opposed to the diffusional contribution, thus reducing the net flux and increasing the observed values of the ratio  $r_{LS,i}^{\beta/\alpha}$ . By contrast, when HCl is used both contributions have the same direction, thus increasing the net flux and decreasing  $r_{LS,i}^{\beta/\alpha}$ .

#### Analysis of the transport number measurements

The analysis of the convective diffusion experiments has led to the conclusion that the effective fixed charge concentration has been reversed due to the polyelectrolyte adsorption.

However, this effect was not observed in the transport number measurements in the presence of lignosulfonate, which showed that the potassium ion behaves as a co-ion. It is therefore necessary to make a further analysis of the transport number measurements in the light of the theory presented above.

Fig. 3 shows the variation of the potassium ion transport number and the Donnan potential with the lignosulfonate concentration in the bathing solution, for different values of the effective membrane fixed charge concentration  $z_m c_m$  and binary electrolyte (KCl) concentration  $c$ . As commented, the addition of lignosulfonate decreases the Donnan potential and increases the co-ion transport number, the effect being very remarkable in the case  $c = 15\text{ mM}$ . However, the observed increase in  $\bar{t}_{K^+}$  after addition of  $1\text{ g l}^{-1}$  of lignosulfonate (solid symbols in top sections of Fig. 3) is larger than predicted by the theory for constant  $z_m c_m$ . This may constitute an additional evidence for lignosulfonate adsorption, even though no charge reversal took place in this case. The low degree of lignosulfonate adsorption observed here is likely to be due to the slow adsorption kinetics<sup>40</sup> together with the lower time needed to run a potentiometric transport number determination compared to the steady-state convective diffusion experiments.

## Summary and conclusions

The convective diffusion of lignosulfonates through charged membranes has been thoroughly analysed both theoretically and experimentally. The transport problem involves important physico-chemical concepts relevant to polyelectrolyte behaviour in electrolyte solutions, Donnan equilibria in multi-ionic systems, and supporting electrolyte concentrations effects in electrochemical systems. These concepts are satisfactorily accounted for by a simple theoretical modelling which considers the problem as an electrodiffusion process of the polydisperse polyelectrolyte through a homogenous charged membrane.

From a practical point of view, the present work constitutes a step forward in polyelectrolyte separation processes. So far, only non-charged porous have been employed and the forced permeation of the different fractions through the membrane was determined by the diffusion coefficient (and then the size) of the polyelectrolyte fraction. By using porous ion-exchange membranes, the effective charge number of the fraction influences its permeation thus enabling a better control of the process. It is shown, however, that polyelectrolyte adsorption (which is not so well controlled) plays a significant role and this demands some caution in the analysis of the transport process.

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