Influence of electrostatic interactions in electrophoretic membrane contactors

Sylvain Galier, Hélène Roux-de Balmann*

Laboratoire de Génie Chimique CNRS UMR 5503, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France
Tel. +33 5.61.55.88.49; email : roux@chimie.ups-tlse.fr

Abstract

In electrophoretic separators, a porous membrane is used to put into contact two flowing liquids between which an electrically driven mass transfer takes place. As far as charged solutes are concerned, the mass transfer can be affected by electrostatic interactions taking place at the membrane solution interface. The influence of these interactions on the solvent and solute transfer is investigated by associating a theoretical and an experimental work, carried out with buffered solutions of different solutes, chosen with respect to their size or electrical charge. Experimental variations of the electroosmotic flux as well as those of the solute concentrations are used to get the values of the characteristic parameters involved in the model. Results obtained with binary solutions are then compared to those obtained with single-solute solutions so as to point out the mass transfer limitation.

Keywords: Membrane contactor; Electrophoresis; Electroosmosis; Mass transfer

1. Introduction

Electrophoresis is an electrically driven operation that constitutes a purification step carried out at the later stage of the downstream process. Because of its high resolution at the analytical scale, different studies were devoted to find out operating modes to scale up electrophoretic separations [1–3].

One of them, free flow electrophoresis, was extensively studied [4–6]. Whilst an interesting resolution was achieved under proper operating conditions [7], the limitation in terms of production capacity was also pointed out as well as the strong relationship between resolution and productivity [8]. On the other hand, electromembrane operations offer the possibility of increasing the productivity without damaging the separation efficiency. The most common is

electrodialysis, in which ion-exchange membranes are used. In that case, however, the main limitation is tied to the size of the solutes, which can not exceed about 500 g/mole.

To overpass this limitation, the replacement of ion-exchange membranes by porous ones was investigated [9–11]. Then the porous membrane acts as a contactor and the separation is achieved with respect to the difference between the mass flow rates of the species, that is fixed by the combination of the different phenomena taking place at the membrane/solution interface.

In this paper the influence of electrostatic interactions is investigated. This study is carried out using a methodology associating a theoretical approach and experimental work. Results obtained with buffered solutions containing two solutes are presented and discussed. The characteristic parameters involved in the model are determined and compared to those previously obtained with single-solute solutions so as to point out the mass transfer limitations.

2. Mass transfer modelling

2.1. Principle of the electrophoretic membrane contactor

The principle of the electrophoretic membrane contactor under study is schematically depicted in Fig. 1. The separation chamber itself is composed of two adjacent compartments delimited by a porous membrane, acting as a contactor between the two liquid streams between which the mass transfer takes place. The voltage, applied in a direction perpendicular to the flows, is the only driving force that makes the charged components fed at the inlet migrating through the membrane from one of the separation compartments to the other. Since solutes of different electrophoretic mobilities are carried through the membrane at different rates, outlet streams are obtained in which the composition is changed compared to that of the feed.

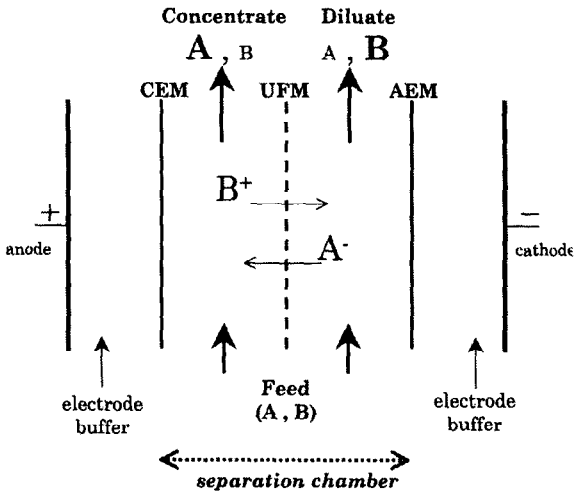

Fig. 1. Principle of electrophoretic membrane contactors. Schematic representation of the separation of two components A and B of opposite charge. UFM: ultrafiltration membrane; AEM and CEM: anion and cation exchange membranes.

2.2. Electroosmotic flux and solute concentration

Two main phenomena resulting from the forced electrical field take place in the system. These are the electromigration of the charged solutes and electroosmosis, which comes from the charges carried by the membrane material. For a solute and a membrane carrying negative charges, these fluxes are oriented in opposite directions. The solute mass balance can be written at steady state, in the solution and in the membrane, using the Nernst–Planck equation, in which the forced convection term is provided by the electroosmotic flux, J_{eo}, which is assumed constant The electroosmotic mobility u_{eo} is defined by Eq. (1), which gives the variation of J_{eo} with the potential gradient E:

$$J_{eo} = u_{eo} . E \qquad (1)$$

A partition coefficient Φ is used to link the solute concentrations in and out of the membrane. Then, for a solute and a membrane carrying negative charges, Eq. (2) is obtained for

the variation of the solute concentration at the outlet in the diluate, C_d, with respect to the parameters of the system [12]:

$$C_d = C_0\left(1 - \frac{u_{eo}E\tau}{d}\right)^{\left[\Phi\left(\frac{u_{mi}}{u_{eo}}-1\right)+1\right]} \quad (2)$$

C_0 is the inlet solute concentration, u_{mi} the absolute value of the solute electrophoretic mobility, τ the residence time inside the chamber that is fixed by the flow rate, and d the thickness of the compartment, i.e., diluate. The value of Φ, ranging between 0 and 1, reveals the strength of the membrane/solute interactions. Decreasing values, meaning a hindered solute transfer through the membrane, reveal stronger interactions. The outlet solute concentration in the concentrate is obtained from the total solute mass balance, i.e.:

$$C_c = 2.C_0 - C_d \quad (3)$$

3. Materials and methods

The electroseparation chamber is 16 cm long, and 2 cm wide, so that the membrane active area is 32 cm^2. The electrode and separation compartments are, respectively, 1 and 0.2 cm thick. The porous membrane used as contactor is a derivated cellulosic membrane made in our laboratory. Its measured hydraulic permeability is equal to 4×10^{-10} $m.Pa^{-1}.s^{-1}$ and its molecular weight cut-off is estimated about 100 kD. Cation- and anion-exchange membranes are used at the anode and cathode side, respectively. Solutions are continuously pumped through the separation compartments, the outlet flow rates being maintained constant and equal. On the opposite, electrode solutions are circulated in a closed loop from a single tank. An automatic system is used for real-time recording of flow rates, conductivities, pH, current, voltage and temperatures. Experiments are carried out at constant temperature and constant current density, ranging from 3 to 22 $A.m^{-2}$. Buffered Tris-Mes solutions at a pH of 8 are used as separation and electrode buffer. The electrical conductivity is equal to 140 and 220 $\mu S.cm^{-1}$ for the separation and electrode solution, respectively. The solute concentration is fixed at 0.1 $g.l^{-1}$. Electrophoretic mobilities of the solutes are determined in the separation buffer by capillary electrophoresis. Different methods are used to get the solute concentration. UV spectroscopy is used for αlacta and Hbb, at 280 and 406 nm, respectively. The concentration of PLGA is obtained by gel permeation chromatography (Superdex peptide column, UV detection at 214 nm).

4. Results and discussion

The influence of the fluid composition on the solvent and solute transfer was investigated. Experiments were carried out with buffered solutions of different compositions, i.e., single-solute solutions and binary mixtures. Table 1 provides the relevant characteristics of the selected solutes, i.e., their molecular weight (size) and electrophoretic mobility (electrical charge). PEG is a neutral solute, the other three being negatively charged. It was formerly mentioned that the membrane used as a contactor carries negative charges. Then, electrostatic interactions, if any, will be repulsive.

Table 1
Characteristics of the solutes used for the experimental study: molecular weight (M_w), isoelectric point (Ip), electrophoretic mobility (u_{mi}). PLGA: poly(L-glutamic) acid; α-lacta: α-lactalbumin; Hbb: bovine hemoglobin

Solute	M_w, kD	Ip	u_{mi}, $m^2.V^{-1}.s^{-1}$
PEG	1	—	0
PLGA	1	3.2	-5.6×10^{-8}
α-lacta	14.2	4.55	-1.85×10^{-8}
Hbb	64.5	7	-0.8×10^{-8}

4.1. Electroosmotic flux

Experimental variations of the electroosmotic flux obtained with buffered solutions containing two solutes, αlacta and PLGA on one hand, αlacta and Hbb on the other hand, are plotted vs. the potential gradient on Figs. 2 and 3, respectively. Corresponding results obtained with single solute solutions are plotted on the same graphs.

One can observe that whatever the fluid composition, the flux first increases with E before reaching a constant plateau value. The origin of this limiting value was previously explained [12]. Moreover, present results show that increasing limiting fluxes are obtained with solutes of increasing electrophoretic mobilities (see Table 1), i.e., increasing electrical charges. On the other hand, the electroosmotic flux obtained with a binary solution is found to be equal to the highest one obtained with single solute solutions. Therefore, the electroosmotic flux value is fixed by the solute which has the highest electrophoretic mobility, i.e., PLGA for the αlacta/PLGA solution and αlacta for the αlacta/Hbb solution. On the other hand, the addition of a neutral solute, PEG, remains without any influence on the electroosmotic flux (results not reported).

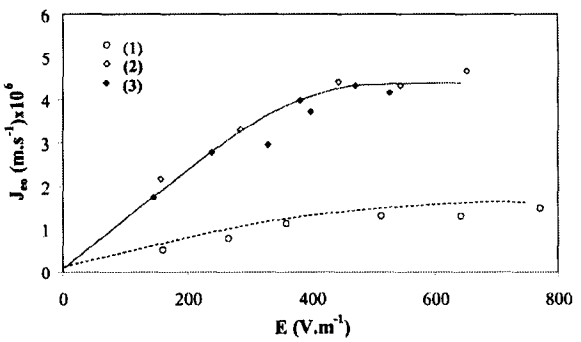

Fig. 2. Variations of the electroosmotic flux vs. the potential gradient. Influence of the fluid composition on the solvent transfer observed with PLGA and α-lacta solutions. (1) buffered solution of α-lacta; (2) buffered solution of PLGA; (3) buffered solution containing α-lacta and PLGA.

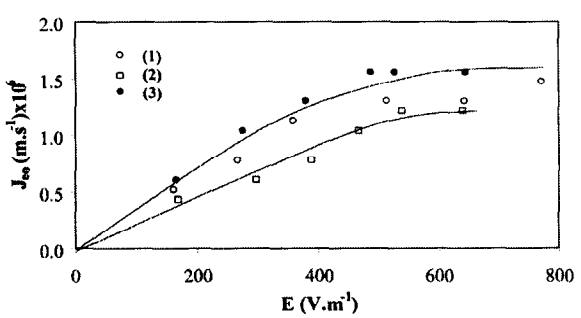

Fig. 3. Variations of the electroosmotic flux vs. the potential gradient. Influence of the fluid composition on the solvent transfer observed with α-lacta and Hbb solutions. (1) buffered solution of α-lacta; (2) buffered solution of Hbb; (3) buffered solution containing α-lacta and Hbb.

4.2. Solute transfer

The solute transfer is characterised by the value of the partition coefficient that is determined by fitting the experimental variations of the solute concentration vs. $E.\tau$ with the ones calculated by Eq. (2). Those values, obtained for binary solutions as well as for single solute solutions, are provided in Table 2.

It was demonstrated that the transfer of PLGA as well as that of α-lacta are governed by electrostatic interactions [12]. For instance, the partition coefficient obtained with PEG, which is a neutral solute having the same molecular weight as PLGA, is equal to 1. These electrostatic interactions are strongly dependent on the apparent electrical charge of the membrane, i.e., on the electroosmotic flux the variations of which were discussed in the former section.

It was shown that the electroosmotic flux obtained with a PLGA/α-lacta solution is equal to that obtained with the PLGA solution. Then, identical partition coefficients are effectively observed for PLGA with both solutions. On the contrary, for α-lactalbumin, the partition coefficient is strongly decreased compared to that obtained with a PLGA-free solution. This

Table 2
Values of the partition coefficient [see Eq. (2)]

Solution	Φ_{PLGA}	$\Phi_{\alpha lacta}$	Φ_{Hbb}
PLGA	0.02	—	—
α-lacta	—	0.8	—
Hbb	—	—	0.02
α-lacta/PLGA	0.02	0.02	—
α-lacta/Hbb	—	0.8	0.02

decrease comes from the enhancement of the electrostatic repulsion due to the increase of the apparent charge of the membrane. Indeed, the electroosmotic flux that reveals this apparent charge is much higher with the PLGA/α-lacta solution than with that containing only α-lacta.

As far as the α-lacta/Hbb solution is concerned, Table 2 shows that the partition coefficient of any solute remains identical to that obtained with single solute solutions. Indeed, since it was observed that the electroosmotic flux is comparable to that obtained with only α-lacta, the electrostatic interactions that set the α-lacta partition coefficient remain constant. On the other hand, whilst the electrophoretic mobility and thus the electrical charge of Hbb is negligible for the conditions investigated (see Table 1), the partition coefficient is very low. This shows that for this solute, the mass transfer is restricted by steric effects. As a result, the electroosmotic flux increase observed with the α-lacta/Hbb solution compared to that obtained with the Hbb solution, that reveals a higher apparent electrical charge of the membrane, has no influence on the Hbb partition coefficient.

5. Conclusions

In this paper, the mass transfer mechanisms involved in electrophoretic membrane contactors were studied by associating a theoretical approach with an experimental study, which was carried out with an original prototype apparatus and buffered solutions of different composition.

The variations of the electroosmotic flux, linked to the apparent electrical charge of the membrane, were studied. The partition coefficient, the value of which reveals the strength of the membrane/solute interactions, was determined by fitting calculated and experimental variations of the solute concentration.

The strong mass transfer limitation due to electrostatic interactions was thus emphasised. For single solute solutions, both solvent and solute transfer were found to be governed by the electrical charge of the solute. Moreover, for binary solutions, it was demonstrated that the electroosmotic flux is identical to that obtained with the solution containing the single solute featuring the highest electrical charge. This increasing flux, which reveals a higher apparent charge of the membrane, was found to lower significantly the solute mass transfer, as far as it is governed by electrostatic interactions.

Finally, it was observed that for some conditions, this enhancement of electrostatic interactions is such that the good selectivity expected from single solute solutions is reduced to zero.

References

[1] K. Hannig, Preparative Electrophoresis, in: M. Bier, ed., Electrophoresis: Theory, Methods and Applications, Vol. 2, Academic Press, New York, 1967, p. 423.

[2] R. Horuk, Preparative Gel Electrophoresis, in: A. Chrambach, M.J. Dunn and B.J. Radola, eds., Advances in Electrophoresis 1, VCH, Weinheim, 1987, pp. 361–380.

[3] P.G. Righetti, M. Faupel and E. Wenisch, Preparative electrophoresis, in: A. Chrambach, M.J. Dunn and B.J. Radola, eds., Advances in Electrophoresis 5, VCH, Weinheim, 1992, pp. 159–200.

[4] M.J. Clifton, N. Jouve, H. de Balmann and V. Sanchez, Conditions for purification of proteins by free-flow zone electrophoresis, Electrophoresis, 11 (1990) 913.

[5] H. Roux-de Balmann and V. Sanchez, Continuous-flow electrophoresis: a separation criterion applied to

the separation of model proteins, J. Chromatog., 594 (1992) 351.
[6] S. Nath, H. Schütte, H. Hustedt and W.D. Deckwer, Application of continuous zone electrophoresis to preparative separation of proteins, Biotechnol. Bioeng., 42 (1993) 829.
[7] H. Roux-de Balmann, R.M. Cerro and V. Sanchez, Purification of bioproducts by free-flow zone electrophoresis: choice of processing parameters, Electrophoresis, 19 (1998) 1117.
[8] F. Dalens, H. Roux-de Balmann and V. Sanchez, Improved operating conditions for preparative separation of proteins by continuous flow zone electrophoresis, Biosep., 5 (1995) 127.
[9] C.F. Ivory, The prospects for large-scale electrophoresis, Sep. Sci. Technol., 23 (1988) 875.
[10] Z.S. Horvath, G.L. Corthals, C.W. Wrigley and J. Margolis, Multifunctional apparatus for electrokinetic processing of proteins, Electrophoresis, 15 (1994) 968.
[11] Z. Liu, Z. Huang, J. Chong, H. Yang, F. Ding and N. Yuan, Continuous separation of proteins by multichannel flow electrophoresis, Sep. Sci. Technol., 31 (1996) 1427.
[12] S. Galier and H. Roux-de Balmann, Study of the mass transfer involved in an electrophoretic membrane contactor, J. Membr. Sci., 194 (2001) 117–133.