Environment Protection Engineering

Vol. 25 1999 No. 1–2

ISABEL M. COELHOSO*, JOÃO G. CRESPO*

MODELLING AND TRANSPORT IN LIQUID MEMBRANE CONTACTORS

The paper deals with carrier-facilitated transport of organic acids and aminoacids in supported liquid membranes. The hydrophobic polypropylene membranes in hollow fibre module were applied in the research. The knowledge about transport mechanism is essential for process optimisation. The quaternary ammonium salt TOMAC was a carrier, which transported lactate from aqueous feed phase to aqueous stripping phase that was diluted sulphuric acid. The accompanying counterbalanced transport of anionic species took place in opposite direction. The mathematical model of coupled transport was presented. The effect of osmotic pressure, hydrophobic and electrostatic effects were taken into account. The equilibrium of reversible reaction between carrier and solute was determined taking into account effect of coupled transport of anionic species in opposite direction. The separation of aminoacids, e.g. phenylalanine and tryptophan, with reversed micelle in TOMAC/hexanol/*n*-heptane system was very effective. The model of mass transport was analysed by taking into account two approaches, i.e. constant and variable partitions. The following resistances to mass transport were assumed in the model, e.g. boundary layer in the liquid phase inside the hollow fiber, resistance to solute diffusion inside the pores filled with liquid phase (membrane), boundary layer in shell side of the tubes. The main aim of the work was detailed understanding of interactions between carrier and solute across liquid membrane. The second aim was to determine hydrophobic and electrostatic effects during the solute transport through structured liquids (reversed micelles). Analysis of the mathematical model of solute transport showed an important role of solute partition in results of simulation. The proposed model makes it possible to involve variation of partition coefficient that is not possible in commonly used classical methods.

INTRODUCTION

Carrier-facilitated transport through liquid membranes has been inspired by the ability of natural systems to selectively pump ions across biological membranes. In liquid membrane systems an immiscible organic phase separates two aqueous phases, the feed and the stripping phases. Solute transport can be enhanced if an extractant, which interacts selectively and reversibly with the solute, is added to the liquid membrane [1].

This lecture reports the use of liquid membranes for extraction of fermentation and pharmaceutical products using different types of carriers. It intends to emphasise the

*Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal.

importance of understanding the transport mechanisms involved in liquid membrane extraction with different carriers and also to discuss a few relevant aspects of the mathematical modelling involved in these extraction processes.

The transport mechanisms involved in the extraction of organic acids by quaternary ammonium salts are discussed and the effect of osmotic pressure differences, through the liquid membrane, on solute transport is evaluated. The selective transport of amino acids using molecular aggregates as reversed micelles in liquid membranes is also presented and the transport mechanisms, considering both electrostatic and hydrophobic interactions, are discussed.

The modelling work analyses two different aspects of extraction using membrane contactors with hydrophobic microporous membranes: i) the importance of using a correct description of solute partition between the feed and the extractant phase (variable partition *versus* constant partition); ii) the correct development of mass transfer correlations.

MATERIALS AND METHODS

MEMBRANE CONTACTOR STUDIES

Liquid-Cel laboratory hollow-fibre modules with Celgard® membranes from Hoechst Celanese were used throughout these studies. Each module has 2.5 cm of internal diameter, contains 2100 hydrophobic polypropylene fibres, 16 cm long, with a nominal internal diameter of 240 μm, nominal thickness of 30 μm, porosity of 0.3 and a nominal pore size of 0.05 μm. Each module provides an effective area of 0.23 m^2. The aqueous feed phase was pumped through the lumen of the fibres while the organic phase flowed in the shell side of the module. Due to the hydrophobic nature of the fibres a slight overpressure (0.2 bar) was applied to the aqueous phase in order to stabilise the interface within the membrane. All the experiments were carried out in co-current flow.

ANALYTICAL METHODS

Concentration of organic acids (lactate and valeric acid) was determined by HPLC. The column used was a Shodex SH 1011 (Showa Denko K.K., Japan) and the eluent sulphuric acid 0.01 N. A refractive index detector (Merck Hitachi, Japan) was employed.The amino acids concentration was also determined by HPLC. The column used was a Merck RP-18 (Merck, Germany) and the eluent was a solution with 75% methanol (v/v) and 25% water (v/v). A UV detector (Merck, Hitachi, Japan) at a wavelength of 257 nm was employed for phenylalanine and tryptophan quantification. The water content of the organic phases (namely the reversed micellar phase) was determined by Karl Fischer titration (Aquapal III, UK). The viscosity of the or-

ganic phases was measured by using a couette type viscometer (Brookfield, model DV-II digital, UK).

RESULTS AND DISCUSSION

TRANSPORT MECHANISMS

Effect of osmotic pressure difference on solute transport

The transport of lactate using as carrier a quaternary ammonium salt (TOMAC) is used to illustrate the importance of understanding the mechanisms involved in solute transport across liquid membranes. The transport of lactate ions from the feed phase to the stripping phase is counterbalanced by an equivalent transport of other anionic species from the stripping to the feed phase through a coupled transport mechanism. A mathematical model for equilibrium was developed assuming an ion-pairing mechanism of transport. The evaluation of the equilibrium constant, K_e, of the reaction between the carrier and lactate allowed a good prediction of equilibrium concentrations for independent extraction and stripping, for a wide range of different experimental conditions [2].

The model predicts that, if lactate transport is exclusively accomplished by an ion-pairing mechanism, a concentration effect can only be achieved with increasing stripping agent concentration. Contrary to the ion-exchange model prediction it can be concluded that it is not worthwhile to increase chloride concentration in the stripping phase above 1 M. For a bulk liquid membrane the ratio of lactate concentration in both phases remains constant for $[Cl^-]_0 = 1.98$ M and for $[Cl^-]_0 = 4.71$ M and it is only 30% higher than the value obtained with $[Cl^-]_0 = 1$ M (Table 1). Similar results were obtained by Drioli and co-workers for phenylalanine extraction also with TOMAC [3].

Prediction of equilibrium is only accurate if both compartments (feed and stripping) have the same molar concentration of salts. For different molar concentrations of salts, in both compartments of the cell, the assumption that transport is exclusively accomplished by an ion-pairing mechanism is not correct and it is necessary to consider the contribution of other mechanisms to ion transport in order to compensate the osmotic pressure difference [4].

In order to verify the existence of alternative mechanisms of transport, the salt concentration difference between the feed and stripping compartments was determined at the beginning of the experiments and at equilibrium, by measuring chloride and lactate in both compartments. The results obtained show that the salt concentration difference at equilibrium is always lower than its initial value. Therefore, a net transfer of sodium chloride occurs from the stripping to the feed compartment. This salt transport was found to increase with increasing initial osmotic pressure difference between the two compartments. The transport of sodium chloride induced by the osmotic pressure difference between the two phases is probably associated with migra-

tion of aqueous 'pockets' across the liquid membrane in order to cancel the osmotic difference.

Table 1

Comparison of experimental and model lactate equilibrium concentrations: effect of initial chloride concentration. Supported liquid membrane, polypropylene membrane 0.1 μm, $[R^+Cl^-]_0 = 0.654$ M

$[La^-]_0$ (M)	$[Cl^-]_0$ (M)	$[La^-]_{f\,exp}$ (M)	$[La^-]_{f\,model}$ (M)	Deviation (%)
0.280	0.276	0.154	0.141	8
0.282	0.998	0.133	0.062	53
0.273	1.950	0.201	0.034	83
0.287	4.710	0.197	0.015	92

Solute transport with reversed micelles

Reversed micelles may provide different environments for solubilization: the reversed micellar water pool and the reversed micellar interface. Depending on the solute structure, polarity and ionisation state we may establish different types of interactions within these environments. These interactions will determine the solubilization site where the solute is hosted and the partition coefficient.

The different type of interactions established between amino acids and the reversed micellar interface can be explored in order to selectively separate amino acids with the same net charge. The results obtained show that even amino acids with very similar isoelectric points, as is the case of phenylalanine (pI = 5.76) and tryptophan (pI = 5.88), can be effectively separated using a reversed micellar system of TOMAC/hexanol/*n*-heptane. The selectivity obtained for resolution of tryptophan/phenylalanine mixtures by extraction with this reversed micellar system was 2.88.

As hydrophobic amino acids (e.g., tryptophan) establish strong interactions with the micellar interface their solubilization depends very much on the interface structure (curvature and bending modulus). This feature can be explored in order to reextract selectively amino acids present in the reversed micellar phase to a receiving aqueous phase. Reextraction with an aqueous phase of a relatively high ionic strength (for example, with a 1 M KCl aqueous solution) causes a reduction of the reversed micellar size, which leads to a squeezing-out of the amino acid from the interface. This procedure is more effective for amino acids solubilized in the micellar interface, as happens with hydrophobic amino acids, than for amino acids solubilized in the micellar water pool or near the interface.

Kinetic Modelling of Extraction Processes

Two basic problems are discussed in this section: the importance of using a correct description of solute partition equilibrium between the feed and the extractant phase (and between the extractant and the stripping phase); and the development of adequate methodologies to obtain mass transfer correlations for extraction in liquid membrane contactors. The first problem was raised because it is quite common to see in the literature the use of constant partition coefficients to describe equilibrium, even when this represents a rather crude simplification. The second question inquires why a method which imposes so many restrictions, as is the case of the Wilson-plot methodology, is still extensively used for development of mass transfer correlations. A new calculation method is, therefore, proposed.

The case study used to illustrate the partition equilibrium problem is the extraction of lactate with TOMAC, as described before. The extraction system used to discuss the development of alternative methods allowing us to obtain mass transfer correlations is the extraction of valeric acid from an aqueous phase using a secondary amine, Amberlite LA-2 [5].

Solute partition equilibrium

Extraction of lactate was performed in a hollow fibre contactor as described in the material and methods section. In order to increase the change in solute concentration, extraction was carried out with recirculation of the feed and organic phases through the module and back into the feed and organic reservoirs.

Table 2

Comparison of the two different approaches, constant P or variable P, to the overall mass transfer coefficient evaluation

Re_t	Re_s	$K_t(10^{-7}$ m/s)		Deviation (%)
		Constant P	Equilibrium curve	
4	2	1.56± 0.31	1.27± 0.25	–23
9		1.11± 0.22	0.89± 0.20	–25
14		1.50± 0.27	1.22± 0.25	–23
18		1.15± 0.29	0.91± 0.22	–26
23		1.46± 0.59	1.14± 0.44	–28
32		1.48± 0.38	1.16± 0.52	–28
36		1.04± 0.19	0.84± 0.19	–24
23	1	1.84± 0.49	1.59± 0.56	–16
	2	0.91± 0.07	1.14± 0.44	–23
	3	1.46± 0.59	0.74± 0.09	–28
	5	1.57± 0.37	1.25± 0.36	–26
	6	1.49± 0.28	1.26± 0.26	–18

Mass transfer coefficients were thus evaluated using the two mentioned approaches [6]:

I. Assuming a constant partition coefficient.

II. Using the equilibrium relation between C_t^* and C_s.

Table 2 compares the values of K_t obtained for these situations. The difference between the calculated values for the overall mass transfer coefficients using either a constant or a variable partition coefficient varies between –16% and –28%. This example illustrates the importance of using a correct description of solute partition equilibrium.

Evaluation of mass transfer correlations

Three individual mass transfer resistances may be considered in contactor extraction processes: (1) the boundary layer resistance in the liquid phase inside in fibres (tube side), (2) the membrane resistance to solute diffusion across the liquid phase wetting the pores and (3) the boundary layer resistance in the shell side liquid phase. The overall resistance, for a hollow fibre system with the membrane wetted by the shell side phase, can be expressed as:

$$\frac{1}{K_t A_i} = \frac{1}{k_t A_i} + \frac{1}{Pk_m A_{lm}} + \frac{1}{Pk_s A_0}, \tag{1}$$

where k_t, k_m and k_s are the individual mass transfer coefficients on the tube side, membrane and shell side, respectively, and A_i, A_0 and A_{lm} are the fibres internal, external and logarithmic mean areas, respectively.

In the present work a Lévèque type equation will be used to correlate both the tube side and the shell side mass transfer coefficients

$$Sh_t = \alpha Sc_t^{b_t} Re_t^{c_t} \left(\frac{d_i}{l}\right)^{1/3}, \tag{2}$$

$$Sh_s = \beta Sc_s^{b_s} Re_s^{c_s} \left(\frac{d_h}{l}\right)^{1/3}, \tag{2}$$

where the subscripts t and s refer to the tube and shell sides, respectively, and α and β are constants. Thus, substituting these equations in Equation (1) allows us to express K_t as a function of four unknown parameters: α, β, c_t and c_s, assuming $b_t = b_s = 1/3$.

When using the Wilson-plot methodology for development of mass transfer correlations the experimental data (C versus t) were fitted and the overall mass transfer coefficients were determined. The inverse of these coefficients were then plotted in two separate graphics, one as a function of $1/Re^{ct}$ (when the tube side Reynolds number is varied) and the other as a function of $1/Re^{cs}$ (when the shell side Reynolds number is varied). From the slopes of these two straight lines the values of α and β were taken.

Table 3 shows the parameter values and the associated errors for a 95% confidence level. It can be seen that for both tube and shell sides the model describes quite

well the experimental results. However, despite the high correlation coefficient (0.987), the errors associated with parameter estimation are considerably high, with errors ranging from 54% to 450%! These excessively high errors question the validity of the methodology, showing that the problem stems from the calculation method. It is not possible to assess its validity in most published works, as the associated errors are not usually stated.

In order to reduce the errors obtained and to prevent the loss of information a single step methodology was developed [7]. K_t was expressed as a function of time and concentration, and then substituted into the model Equation (1), thus achieving a single analytical expression. By fitting all the experimental values of C versus t to the model equation the parameters α, β, c_t and c_s were obtained.

Table 3 shows that this method produces parameter values in a totally different range, showing higher exponent values for the Reynolds numbers. The errors are drastically reduced ranging from 15 to 22%. This drastic reduction, roughly of 20 times, of the errors associated with the estimated parameters when using the one-step methodology and the different results obtained by these two methods, lead us to conclude that the Wilson-plot method may also be inaccurate. The one-step calculation method developed can easily be applied giving the currently available mathematical tools that enable the analytical manipulation of equations and fittings with complex expressions.

Table 3

Parameter values and errors using the Wilson-plot methodology and using a one-step calculation

Method	Parameter	Value and error	% Error	r^2
Wilson-plot	c_t	0.558±1.277	229	0.987
	c_s	0.355±1.414	398	
	α	0.305±0.164	53.8	
	β	1.487±6.691	450	
One-step	c_t	0.914±0.136	14.9	0.997
	c_s	0.697±0.136	19.5	
	α	0.272±0.047	17.3	
	β	3.364±0.739	22.0	

CONCLUSIONS

Liquid membranes are a unique tool for selective transport of desired solutes from complex mixtures. The industrial future of liquid membranes will depend very strongly on the ability to identify and synthesise selective carriers or receptors with

the potential to achieve recognition of individual solutes. Therefore, the trend will be the development of supramolecular chemistry with the aim of obtaining very selective carriers, in some cases with the ability for chiral recognition.

The first part of this communication discusses the importance of a detailed understanding of the carrier–solute interactions and the mechanisms involved in solute transport across liquid membranes. The first case study presented was a rather non-specific interaction between a quaternary amine ion-exchanger and lactate. It was our aim to demonstrate that when an organic phase with some permeability to water is used, osmotic pressure differences across the liquid membrane may have to be considered for a correct description of solute transport. This situation is rather common and the analysis presented can be applied to similar situations. The other case study presented – transport with reversed micelles – shows how structured fluids (as reversed micelles) can be used for selective transport by making use of electrostatic and hydrophobic interactions with the solutes.

The second part of this work brings to the discussion a few aspects related to modelling of liquid membranes. The discussion presented aims to call attention to the importance of using a correct description of solute partition, specially when it is getting common the use of constant partition coefficients, even when this is a wrong assumption. The proposed one-step method may represent a useful tool for development of mass transfer correlations. Amongst other advantages, this approach makes it possible to consider a variation of the partition coefficient which was not possible in the case the Wilson-plot method was applied, where all the variables but the Reynolds number have to be considered constant.

Acknowledgements

The authors would like to acknowledge Dr. Margarida Cardoso and to the PhD student Mr. Rui Viegas. The authors also acknowledge the collaboration with Prof. José Ramon Alvarez, Dr. Susana Luque and Dr. Marino from University of Oviedo, Spain, who encouraged the development of new methodologies for evaluation of mass transfer correlations.

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