Prediction of overall mass transfer coefficients in continuous dialyzers: comparison of pseudo steady state approximation and unsteady state solution

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Abstract

This work describes the determination of carboxylic acid overall mass transfer coefficients in a circulating flow experimental set-up composed of a flat plate dialyzer and a concentrate reservoir. Sodium acetate and sodium propionate were used as the sodium salts of carboxylic acids. By referring to the model generated concentrate reservoir concentration vs. time data, we focused our attention on the quantitative justification of the previously published equation of ours that could be implemented as a new tool in the determination of overall mass transfer coefficients in dialysis processes. Furthermore, the present study was undertaken for the comparison of unsteady state case, i.e. rigorous solution, predicted overall mass transfer coefficients against a simpler expression based on a pseudo steady state approximation. Contrary to the concentrate side, single pass flow was used on the diffusate side where the receiving liquid was deionized water. It was found that the overall mass transfer coefficient values, K for both solutes increased with the increase of the flow rate. The K values calculated by rigorous solution, i.e. taking into account the unsteady state effects, were always higher than those obtained via pseudo steady state approximation.

Keywords: Overall mass transfer coefficient; Dialysis; Unsteady state; Modeling; Recirculation

1. Introduction

Membranes are being used in diverse applications, amongst others, separation, purification, enriching, recovery, pollution control, controlled release, sterilization and hemodialysis makes them indispensable. The accurate estimation of rates of mass transfer between two phases has been the subject of substantial portion of the chemical engineering literature, and membrane

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processes are no exception. The basic work, describing a model for mass transfer of solutes in membrane modules used as artificial kidneys is that of Villarroel et al. [1]. With the development of new membranes having better separation efficiency, new membrane processes such as membrane contactors and membrane reactors are becoming common unit operations in process engineering [2]. Furthermore, new hybrid membrane separation technologies, such as seeded microfiltration, might find interesting applications in the removal of ionic species from aqueous solutions [3]. In the present study we focus our attention on a strategy to deal with the determination overall mass transfer coefficients (cm/s), K in dialysis processes. Nagy [4] presented explicit mathematical expressions for the calculation of the concentration profile in the membrane and the mass transfer rates with a quasi-analytical approach. Yeh and Chang [5] showed that considerable improvement of mass-transfer rate in a parallel-plate dialyzer module of fixed dimensions is accessible by using double passes, instead of single pass, where the mass transfer is dominated by external film. For the system of a continuous dialyzer at steady state, Palaty et al. [6] developed a model that takes into account a variable flow of liquid along the membrane. Their procedure enables to calculate the basic transport characteristics of dialysis processes. Özdural and Alkan [7] proposed an explicit equation through a rigorous analysis where unsteady state mass transfer is taken into account, and their equation allows the determination of K values in continuous dialyzers through the implication of experimental data gathered in recirculation systems. If the hydrodynamic conditions within a single pass membrane module mimic that of recirculation system than the so calculated K value by Özdural–Alkan equation becomes applicable to single pass systems as well. This methodology is also relevant in evaluating mass transfer

characteristics in membrane contactors [8], and for the determination of kinetics coefficients in packed-bed reactors [9].

Qi and Cussler [10] developed a model to simulate the operation of a microporous hollow fiber membrane contactor in gas absorption processes. As an extension of this work, D'Elia et al. [11] developed a similar model for liquid–liquid extraction for microporous hollow fibers with recirculation of the streams on both sides of the membrane. The mathematical analysis of Qi and Cussler [10] and D'Elia et al. [11] were based on the assumption that the membrane module works close to the steady state. Trebouet et al. [12] observed that the analytical solution is then possible with pseudo steady state approximation.

In this work, contrary to the above mentioned system of Trebouet et al. [12] where fluid streams recirculated on both sides of the membrane, recirculation at the concentrate side only is envisaged. Diffusate side liquid, i.e. deionized water, is introduced in a single pass fashion with a relatively high velocity. Under such conditions, it can be assumed that the diffusate side solute concentration becomes negligible mainly due to the short travel path of solutions within the present flat-plate dialyzer. As long as these conditions hold and formulating with pseudo steady state approximation, the model proposed by Trebouet et al. [12] leads to Eq. (1). This equation might be employed in various types of membrane separation processes for the determination of K values if pseudo steady state conditions hold [8].

$$K \approx \frac{Q}{wL} \ln \left[\frac{1}{1 + \ln(C_{in}^{c}/C_{0}^{c})^{\tau_{res}/t}} \right] \quad (1)$$

where Q is the concentrate side recirculation rate (cm³/s), w is the membrane width (cm), L is the membrane length (cm), h is the dialyzer concentrate side chamber height (cm), t is the time (s), τ_{res} ($\tau_{res} = V^{c}/Q$) is the residence time in the concentrate reservoir (s), and V^{c} is the

reservoir volume (cm^3). Fig. 1 illustrates that C_{in}^c is the time dependent concentrate reservoir solute concentration (mmol/cm^3) which is equal to the dialyzer inlet concentration, C_1^c. The concentrate reservoir solute initial concentration is C_0^c (mmol/cm^3).

It might be interesting to note that the same expression, i.e. Eq. (1), was derived for hemodialysis studies by Özdural and Piskin [13] in 1978. For the case of unsteady state mass transfer within the membrane module, Eq. (2) allows the determination of K values in continuous dialyzers which was proposed by Özdural and Alkan [7]. Recently, Loureiro [8] showed that Eq. (2) can also be derived by the employment of method of characteristics, where τ_{mod} ($\tau_{mod} = hwL/Q$) is the residence time (s) in the concentrate side of dialyzer.

$$K = \frac{Q}{wL} \ln \left[\frac{(C_{in}^c/C_0^c)^{-\tau_{mod}/t}}{1 + \ln(C_{in}^c/C_0^c)^{\tau_{res}/t}} \right] \qquad (2)$$

The significance of this work is three-fold. First, we focused our attention on the quantitative justification of Özdural–Alkan equation, i.e. Eq. (2) that could be implemented as a new tool in the determination of overall mass transfer coefficients in dialysis processes. Second, for the same system and operating parameters, we compared the K value predictions of Eqs. (1) and (2). Finally, the present study was undertaken with the aim of determining dialyzer overall mass transfer coefficients where two different carboxylic acid sodium salts were used as the concentrate side solution.

2. Numerical solution strategies for the prediction of the change of concentrate reservoir concentration with time in recycling dialyzers

Fig. 1 shows the schematic lay out of the experimental set-up where a membrane module with recycle system is envisaged. A stream is
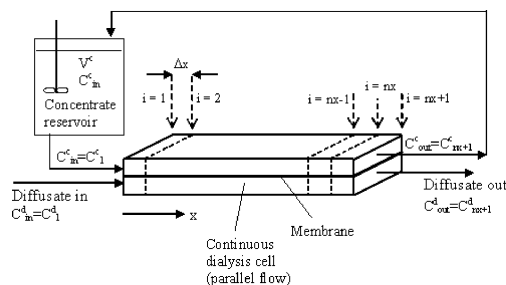

Fig. 1. Schematic layout of the dialyzer.

taken from the reservoir, fed to the membrane module, and then recycled back to a reservoir. The purpose of this section is to present two alternative methodologies to be used for the prediction of concentrate reservoir C_{in}^c versus t profiles. With referring to Fig. 1, let us consider a flat plate membrane dialyzer where solution to be dialyzed (concentrate) circulates on one side of the membrane module and returns to the reservoir. Diffusate phase flows in the other side of the membrane with a single pass fashion.

Let us assume:

(a) The concentrate composition, C^c (mmol/cm^3) in the continuous dialyzer is a function of distance x (cm) and time t (s) only.

(b) Perfect mixing in concentrate reservoir where C_{in}^c is both the concentrate reservoir concentration and the dialyzer concentrate side inlet concentration (mmol/cm^3).

(c) Diffusate inlet concentration C_{in}^d (mmol/cm^3) is zero. The diffusate concentration within the dialyzer, C^d (mmol/cm^3) can be neglected as compared with C^c for the following cases: short travel path of solutions within the dialyzer and/or slow flux of solute molecules through the membrane and/or high diffusate phase velocity within the dialyzer.

(d) Axial diffusion (x direction) in the concentrate side of the flat plate dialyzer are neglected due the high linear velocity attained under experimental conditions.

It is not difficult [14] to show that Eq. (3) gives the governing partial differential equation of the membrane module of the present system.

$$\frac{\partial C^c}{\partial t} + \frac{Q}{hw}\frac{\partial C^c}{\partial x} + \frac{K}{h}C^c = 0 \tag{3}$$

For the concentrate reservoir shown in Fig. 1, a mass balance gives

$$\frac{dC_{in}^c}{dt} = \frac{1}{\tau_{res}}(C_{out}^c - C_{in}^c) \tag{4}$$

C_{out}^c is the concentrate reservoir inlet concentration (mmol/cm^3), which is equal to the dialyzer outlet concentration, C_{nx+1}^c.

When the dialyzer concentrate side residence time, τ_{mod}, is small and/or the overall mass transfer coefficient is low then there shall be a slight change between the dialyzer inlet and outlet concentrations. On the other hand for recirculated systems, cumulative effect of this slight change shall be reflected as visible changes in the reservoir concentration. Özdural and Alkan [7] employed a rigorous analysis for the simultaneous solution of the partial differential equation given by Eq. (3) and the ordinary differential equation given by Eq. (4) so as to predict the time change of concentrate reservoir concentration. From now on we shall call this method as "complete numerical solution", where implicit scheme finite differences numerical analysis technique was employed. Initial and boundary conditions for recirculating dialyzer system are given below where i and j are the x and t panel indexes used in the numerical solution, respectively.

I.C. $t = 0$ for all x in the dialyzer; except at $x = 0$, $t = 0$ for concentrate reservoir
B.C. for $t > 0$ $x = 0$ $C_{1,j}^c = C_{in}^c$
$x = L$ $C_{nx+1,j}^c = C_{out}^c$

We have approximated the above given B.C. at $x = L$, i.e. at $nx + 1$ by linear extrapolation of values at $i = nx - 1$ and $i = nx$.

On the other hand, Özdural [14] showed that if τ_{mod} is small and/or the mass transfer rate through the dialyzer is not very fast, starting with Eqs. (3) and (4) we end up with the following first order ordinary differential equation. The solution of Eq. (5) gives time change of concentrate reservoir concentration. In this work fourth order Runge–Kutta method is used for the numerical solution of Eq. (5).

$$\frac{dC_{in}^c}{dt} = (C_{in}^c/\tau_{res})$$
$$\times \left\{ [\exp(-wLK/Q)](C_{in}^c/C_0^c)^{-\tau_{mod}/t} - 1 \right\} \tag{5}$$

For the same system and operating parameters, we should obtain a realistic agreement between C_{in}^c versus t profile predictions of the two independent strategies mentioned above, i.e. those of Özdural [14] and Özdural and Alkan [7], in order to consider their appropriateness in dialyzer mass transfer assessment studies.

3. Experimental

Dialysis experiments were conducted at 20°C with a flat plate dialyzer ($h = 0.1$ cm, $w = 4$ cm, $L = 20$ cm), using Cuprophan PT 150 (Enka AG, Germany) cuprammonium cellulose membrane. The membrane dry thickness was 12.3 µm with a nominal MW cut-off value of 10 kDa. Polypropylene mesh was used to hold the membrane within the module. The well mixed concentrate solution reservoir volume, V^c was 500 cm^3. Sodium acetate and sodium propionate were used as the sodium salts carboxylic acids (Merck, Germany). The initial concentrations of aqueous solutions of solutes on the concentrate reservoir were equal to 0.2 M. The solute concentrations were monitored by a conductivity probe (Tacussel, France) and were determined by a calibration curve. Three different concentrate side recirculation rates were used (100, 200 and

$400 \, \text{cm}^3/\text{min}$). Contrary to the concentrate side, single pass flow was employed on the diffusate side where deionized water was used as the receiving liquid. In all experiments diffusate side flow rate was kept as $400 \, \text{cm}^3/\text{min}$. Concentrate side liquid recycling and deionized water streaming in a single pass fashion at the diffusate side were carried out by peristaltic pumps (Cole-Parmer, USA).

4. Results and discussion

Fig. 2 illustrates the complete numerical solution model [7] determination of overall
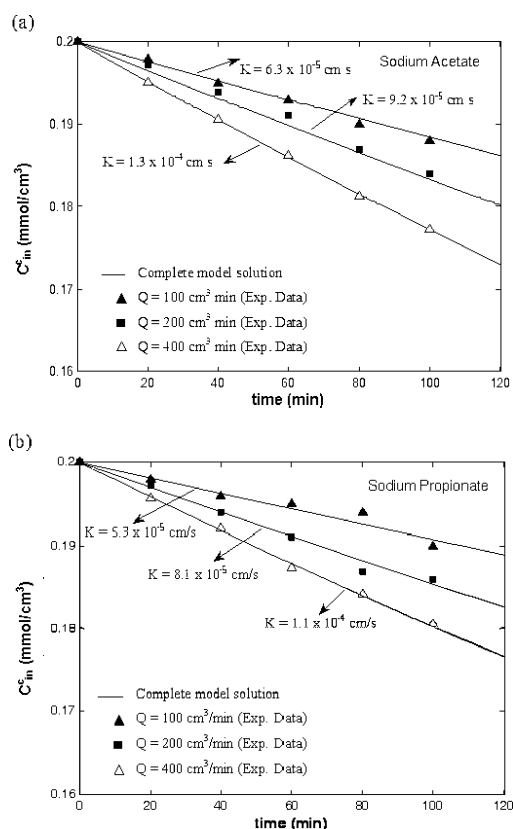

(a)

(b)

Fig. 2. Time change of concentrate reservoir concentration with recirculation rate, and comparison of complete model predicted profiles with experimental data. Test solute: (a) sodium acetate and (b) sodium propionate.

mass transfer coefficients for the concentrate recirculation rates of 100, 200 and $400 \, \text{cm}^3/\text{min}$ where diffusate side (deionized water) flow rate kept constant at $400 \, \text{cm}^3/\text{min}$. Fig. 2(a) and (b) gives the change of K values with Q for sodium acetate and sodium propionate, respectively. Model output values of the reservoir concentration versus time data are generated by substituting different K values into the model until the predicted profiles and experimental data agree. The overall mass transfer coefficient increases with the increase of the flow rate if other parameters are kept constant. This can be attributed to the decrease of concentrate size film mass transfer resistance with the increase of flow rate. It was found that under similar system and operation parameters, sodium acetate K values were nearly 20% higher than those of sodium propionate as a consequence of the larger molecular weight of the latter. Since the determination of K values via complete numerical solution depends on the model predicted C_{in}^c versus t profiles, for the same system and operating parameters, C_{in}^c versus t profile predictions are also carried out by a completely independent strategy [14] as mentioned in Section 2, in order to consider its appropriateness in dialyzer mass transfer assessment studies. Fig. 3 shows the comparison of Özdural and Alkan complete numerical solution [7] and Özdural [14] methodologies for C_{in}^c vs. t prediction by employing the same parameters of that of Fig. 2 where the Q value was kept at $400 \, \text{cm}^3/\text{min}$. The comparison of the model predicted C_{in}^c values at various dialysis times for sodium acetate and sodium propionate are illustrated in Fig. 3(a) and (b), respectively. This figure clearly illustrates that C_{in}^c versus t profile predictions of the two models completely agree with each other. As a consequence, for the present case one might consider that, if the system and operating parameters and the K value are the same, then C_{in}^c versus t profile predictions of the two models
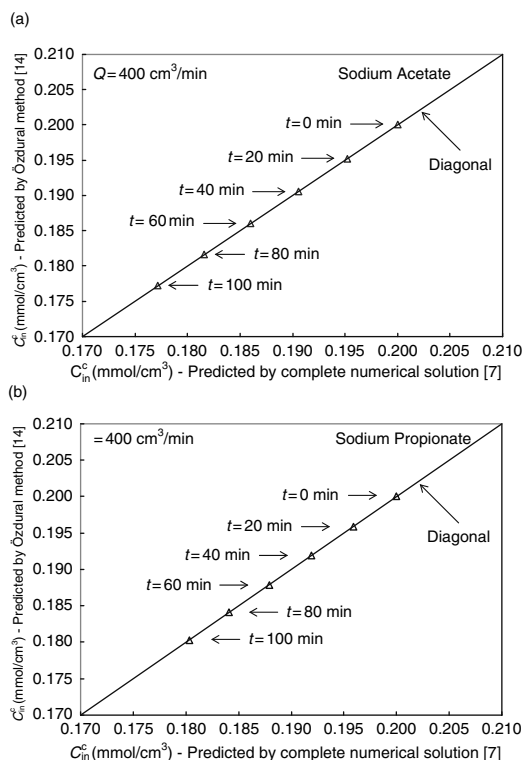
Fig. 3. Comparison of Özdural and Alkan [7], i.e. complete numerical solution, and Özdural [14] methodologies for reservoir concentration predictions at recirculation rate of 400 cm³/min. Test solute: (a) sodium acetate and (b) sodium propionate.
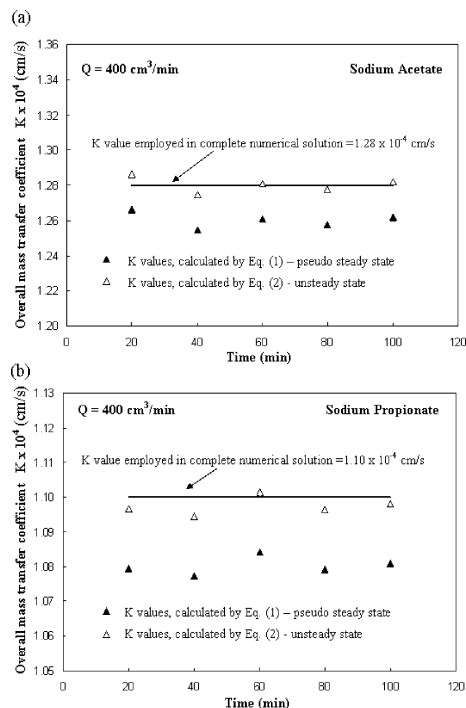

Fig. 4. Comparison of *K* values calculated through pseudo steady state approximation and unsteady state solution for the recirculation rate of 400 cm³/min where experimental data is substituted into Eqs. (1) and (2), respectively. Test solute: (a) sodium acetate and (b) sodium propionate.

can interchangeably be used during dialyzer mass transfer assessment studies. Thus it becomes immaterial which model mentioned in this work is used during the *K* value prediction procedure. Fig. 4(a) and (b) shows the comparison of the *K* value predictions of Eqs. (1) and (2) through the use of experimentally determined sodium acetate and sodium propionate C_{in}^c versus *t* data, respectively, for the recirculation rate of 400 cm³/min. The solid lines in Fig. 4(a) and (b) represent the complete model predicted *K* values obtained via the procedure explained in Fig. 2. When "*t* and the corresponding C_{in}^c" data were gathered from the output of the model solution, then the *K* value obtained by other means, such

as through Eq. (1) or (2) should be consistent with the *K* value that was employed in the complete model. With this criterion in mind, Fig. 4 shows that for the same parameter values, Eq. (2), i.e. unsteady state solution, meets the above mentioned constraint perfectly whereas Eq. (1), i.e. pseudo steady state approximation systematically estimates lower *K* values. Similar results were obtained for recirculation rates of 100 and 200 cm³/min. The *K* value predictions of the pseudo steady state solution are close to the unsteady state model predictions, yet the superiority of the unsteady state solution over the pseudo steady state approximation is evident. Comparison of the numerators of Eqs. (1) and (2) reveals that the difference between the *K*

value predictions are expected become more pronounceable when the dialyzer concentrate side residence time, τ_{mod} is large, and/or when the K value is evaluated at the initial stages of the experimentation.

5. Conclusion

The present study was undertaken for the comparison of unsteady state solution predicted overall mass transfer coefficients in continuous dialyzers against a simpler expression based on a pseudo steady state approximation. It was concluded that Özdural–Alkan equation, i.e. Eq. (2) obtained through unsteady state solution [7], improves the accuracy of the dialyzer overall mass transfer coefficient predictions over pseudo steady state approximation given by Eq. (1). Furthermore, Eq. (2) might become a useful tool in the K value calculations of other membrane separation processes such as membrane contactors. During the experimental phase of this study dialysis of sodium acetate and sodium propionate were carried out in flat plate dialyzer where membrane overall mass transfer coefficients for both solutes increased with the increase of the flow rate.

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