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Determination of mass transfer coefficient of a cross-corrugated membrane reactor by the limiting-current technique

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Abstract

We report mass transfer coefficient correlations, at low Reynolds numbers for a novel cross-corrugated membrane reactor, which is being developed for a number of processes, most notably phase-transfer catalysed reactions. The presence of Tollmien–Schlichting (T–S) waves saw a noticeable enhancement in mass transfer, giving characteristics usually only found in turbulent flow. Correlations for the channel wall and the channel corrugations are given in terms of dimensionless Sherwood numbers:

$$Sh_{\mathrm{CW}} = 0.0209 Re^{0.7675} Sc^{0.333} \quad (200 < Re < 2300),$$

$$Sh_{\mathrm{COR}} = 0.2477 Re^{0.489} Sc^{0.333} \quad (200 < Re < 2300).$$

1. Introduction

1.1. Membrane reactors

Since the majority of natural biochemical systems contain reactions involving membrane-bound enzymes, it seems only natural for scientists to try to emulate such efficient methods. Cells have been successfully grown in hollow fibre membrane bioreactors, giving distinct advantages over traditional fermenters [1]. Process runs and downtimes between runs are shorter, equipment sterilisation much easier, and scale-up methods much simpler. The hollow fibre membrane provides a large surface area per unit volume in which control of heat and mass transfer is far superior to the equivalent fermentation unit.

The term *membrane reactor* is a relatively new one, first appearing in chemical literature around 1979 [2]. Since then, much confusion has arisen concerning its definition. It is probably most acceptable to define membrane processes *functionally*, rather than *structurally*. There are for instance, PTFE, PVDF, nylon and cellulose acetate membranes amongst others which can function identically in a given membrane reactor. The term *reactive membrane* is applied where the membrane serves merely as a catalyst support, while the term *membrane reactor* is reserved for cases in which the membrane has the unique ability to *organise*, *compartmentalise*, and to *separate*.

Flat-sheet immobilised enzyme reactor systems have been developed for amino acid and penicillin biotransformations, with the reactor modules consisting of the required enzyme attached to multiple layers of microporous PVC–silica membrane [3]. The obvious advantage the hollow fibre has over the flat sheet is one of mass transfer. A liquid flowing across a series of tubes will break up boundary layers, giving it less resistance to mass transport. Corrugating a flat sheet however, will also allow these intrinsic boundary layers to be disrupted.

Of close relevance to this field of research is in the development of polymer film compact heat exchangers. Investigations have been performed by Jachuck and Ramshaw [4] using cross-corrugated films of identical dimensions to those studied here.

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Nomenclature

C	bulk reactant concentration (kmol m^{-3})
C_0	reactant concentration at the electrode (kmol m^{-3})
d_e	equivalent diameter (m)
D	diffusivity (m^2 s^{-1})
i	current density (A m^{-2})
i_l	limiting current density (A m^{-2})
F	Faradays constant
k	mass transfer coefficient (m s^{-1})
Nu	Nusselt number
Re	Reynolds number
Pr	Prandtl number
Sc	Schmidt number
Sh	Sherwood number
St	Stanton number
V	volume (m^3)
x	distance from leading edge (m)

Subscripts

CW	channel wall
COR	corrugations

Greek symbols

ν	kinematic viscosity (m^2 s^{-1})
μ	viscosity (kg $m^{-1}s^{-1}$)

The aim of this investigation is to study the flow patterns across the corrugated surfaces, to detect dead spots in the cell design, and to determine localised mass-transfer coefficients across the membrane. The results are given herein.

2. Reactor configuration and experimental

2.1. Limiting current technique

Mass transfer studies prior to the 1960s relied on a method of measuring the rate of decrease in thickness of a surface dissolving in a fluid. The limiting current technique brought an easier and altogether more efficient way, allowing for rapid, precise measurement of transfer rates, without physically altering the surface to be studied. The theory of the process is well documented and will not be discussed here [5]. Ions in the bulk solution move towards the electrode by diffusion, and when this transport process becomes the rate-limiting factor, a *limiting-current* is observed. By varying the voltage applied, the current also varies, until it reaches its limit, the maximum rate at 100% current efficiency, at which the reaction can proceed. This rate is dependent on the composition and transport properties of the electrolyte solution, and on the hydrodynamic conditions at the electrode surface. It follows that by keeping the former constant, mass transfer coefficients at different flow configurations can be determined for a range of flowrates.

Having designed the membrane reactor as a cross-flow unit where the corrugations of each alternate membrane lay at 90° to one another, one can assume that there are two distinct surfaces over which the fluid will flow. The fluid on one side of the membrane has a smooth channel to run along, and on the other side, the fluid flows over a series of peaks and troughs. It was therefore necessary to conduct identical experiments for both surfaces, and compare the mass-transfer characteristics.

The cell built to emulate the membrane reactor was identical in size and shape, the only difference being in that the 'membranes' were constructed of glass plates, shown in Fig. 1, giving visibility throughout the unit. The corrugations of the membranes were 1.3 mm in height, with 2 mm from peak to peak. A dye was injected at various inlet points along the width of the plate to ensure no dead spots existed both at the extreme edges and at the corners of the membrane. No dead spots were detected.

Fig. 2 illustrates the layout of the apparatus, consisting of 1 l reservoir of electrolyte feeding the cell via a centrifugal pump, and returning to the reservoir. An EG&G Princeton Applied Research VersaStat was used to conduct the electrolysis process under linear sweep voltammetry. The data was logged using EG&G Model 270 Research Electrochemistry Software.

A frequently used reaction system for this technique is the cathodic reduction of ferricyanide

$$\mathrm{Fe(CN)_6^{-3}} + \mathrm{e^-} \rightarrow \mathrm{Fe(CN)_6^{-4}} \tag{1}$$

One must note that since the study is of the reaction at the cathode, this should be smaller than the anode, to ensure the limiting reaction does indeed occur at the cathode.

The electrolyte consisted of the following components:

0.3 M KCO_3	supporting electrolyte.
0.02 M $K_3Fe(CN)_6$	ferricyanide to be cathodically reduced.
0.05 M $K_4Fe(CN)_6$	ferrocyanide in excess.[1]

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[1] As the reaction is reversible, an excess of anodic reactant is required to ensure the limiting current is at the cathode.

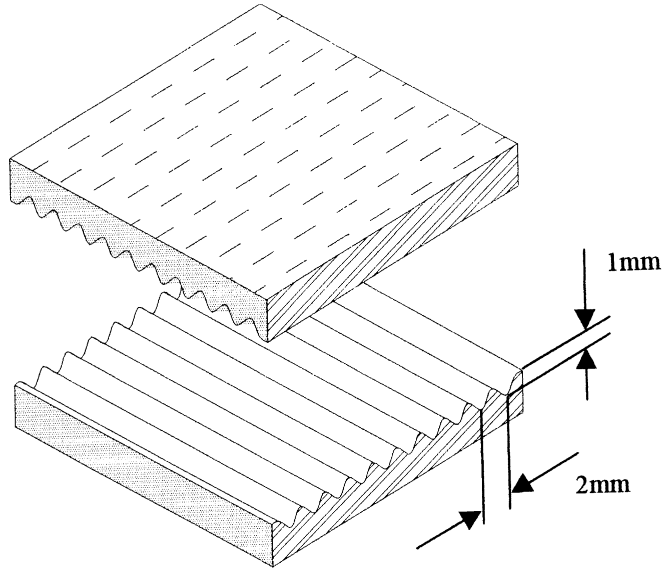

Fig. 1. Glass membrane plates.

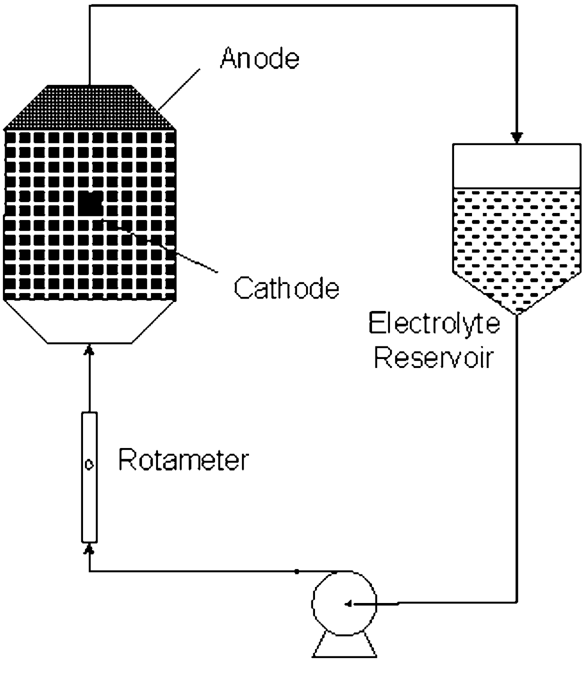

Fig. 2. Flow cell arrangement.

The nickel cathode was pressed into one of the glass plates to take the shape of the corrugations, and both it and the anode, also nickel, were polished with emery cloth. The back of the cathode was previously coated with insulating paint, and an electrical connection established at the side edge to avoid interference to the flow pattern. Nitrogen was bubbled through the electrolyte to expel dissolved oxygen.

At a constant flowrate, a slow linear sweep of potentials was applied to the cell, and the corresponding currents measured. As the reaction proceeded, the current increased to a maximum, the limiting current,

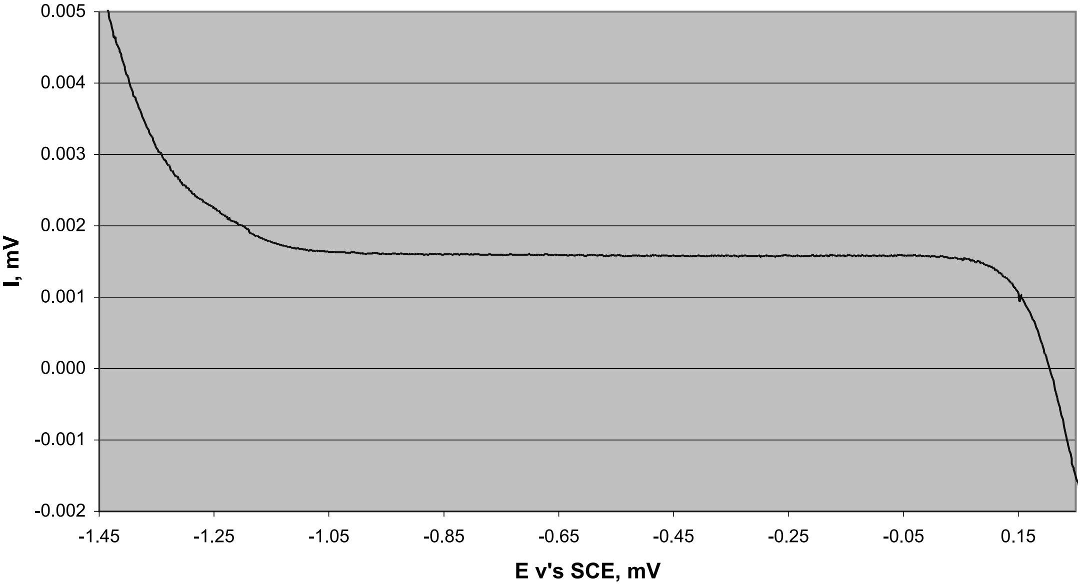

Fig. 3. The limiting current plateau region for ferricyanide reduction at corrugated nickel electrodes.

where it remained constant as the cathodic potential increased. The limiting current plateau extended over a range of mV as shown in Fig. 3. A further increase in potential caused the current to begin increasing once more. At this point, as well as the ferricyanide reaction, hydrogen gas was evolved. Once the cell voltage range at which the limiting current occurred was identified, the process was repeated over a range of flowrates, and in different positions over the surface of the membrane.

3. Results and discussion

Local mass-transfer rates were calculated directly from Faraday's law, stating that the current density at the electrode i is proportional to the reacting ion flux N_i

$$s_i i = -nFN_i, \tag{2}$$

where s_i is the number of ions participating in the transfer of n electrons to or from the electrode. As the mass transfer coefficient k can be defined by

$$N_i = k(C_0 - C_\mathrm{b}) \tag{3}$$

and as the concentration of the reacting species at the cathode can be assumed to be approaching zero, it follows that:

$$k = \frac{s_i i_1}{nFC_\mathrm{b}}. \tag{4}$$

Dimensionless Sherwood and Stanton numbers may then be calculated by

$$Sh = \frac{kd_\mathrm{h}}{D} = \frac{i_1 d_\mathrm{h}}{nFDC_\mathrm{b}}, \tag{5}$$

$$St = \frac{Sh}{ReSc} = \frac{i_1}{nFC_\mathrm{b} v_\mathrm{b}}, \tag{6}$$

where

$$Re = \frac{d_\mathrm{h} v_\mathrm{b}}{v} \tag{7}$$

and

$$Sc = \frac{v}{D}. \tag{8}$$

A correlation relating the three dimensionless parameters can then be established. Sieder and Tate [6] first used a relationship of dimensionless groups to determine heat transfer coefficients in tubes

$$Nu = Nu(Re, Pr, l/d, /\mu_\mathrm{b}/\mu_0), \tag{9}$$

where μ_b is the viscosity at an average fluid temperature, and μ_0 is the viscosity at the tube wall temperature.

To achieve the analogous relationship that exists between heat and mass transfer, one merely needs to substitute one dimensionless group with another to convert a heat-transfer correlation to the corresponding mass-transfer correlation [7]. The correlation depends largely on which flow regime exists in the cell, ranging from simple laminar flow, laminar flow with complications, free and mixed convection, turbulent forced convection, oscillating flows, stirred cells, convection by gas evolution, and particulate [5]. The system reported attempts to evaluate the use of corrugations to promote turbulence in regions of low flow, and is unusual in that as the channels are made up of two identical surfaces, one rotated 90° from the other, their effective flow path is entirely different. The fluid on one side of the membrane has a smooth channel to run along, and on the other side, the fluid flows over a series of peaks and troughs. It was therefore necessary to conduct identical experiments for both surfaces, and treat the results using the two types of correlation for laminar flow.

3.1. Correlation for flow along the channel wall

The Leveque type relationship, valid for parallel flows, was used to correlate mass transfer along the surface of the membrane channels at Reynolds numbers between 200 and 2300

$$Sh = C\left(ReSc\frac{d}{x}\right)^{0.333}. \tag{10}$$

When plotted, the correlation did not fit the Leveque equation, but did fit an equation corresponding to a system exhibiting turbulent characteristics

$$Sh_{\mathrm{CW}} = 0.0209Re^{0.7675}Sc^{0.333}. \tag{11}$$

Furthermore, Fig. 4 shows that the Sherwood number is independent of the distance from the leading edge of the membrane.

On analysis, the correlation is equivalent to other published correlations of mass transfer in turbulent flow in channels of similar dimensions to those used in this study [8–10]. Clearly the peaks and troughs, across which the fluid flows, act as turbulence promoters for a system with such low flowrates.

3.2. Correlation for flow across the channel corrugations

The boundary layer type correlation, used for transverse velocity components, in our case the troughs and peaks of the membrane, initially corresponded to laminar flow characteristics

$$Sh = CRe^{0.5}Sc^{0.333}. \tag{12}$$

Fig. 5 shows a laminar boundary layer relationship, which initially looks to fit perfectly well. On further analysis however, a change in electrolyte viscosity alters the intercept of the slope by over 26%. By treating the system as turbulent, the data in Fig. 6 shows a good agreement for Reynolds numbers between 200 and 2300 of

$$Sh_{\mathrm{COR}} = 0.2477Re^{0.489}Sc^{0.333}. \tag{13}$$

The mass transfer correlation showed that the laminar flow thought to exist at low flowrates does not fit this supposition. In fact, it is more likely that the irregular flow path caused by the corrugations gives a more turbulent flow. The theory has been explained in a publication describing the enhancement in mass transfer as being due to a self-sustaining oscillatory flow [11]. The

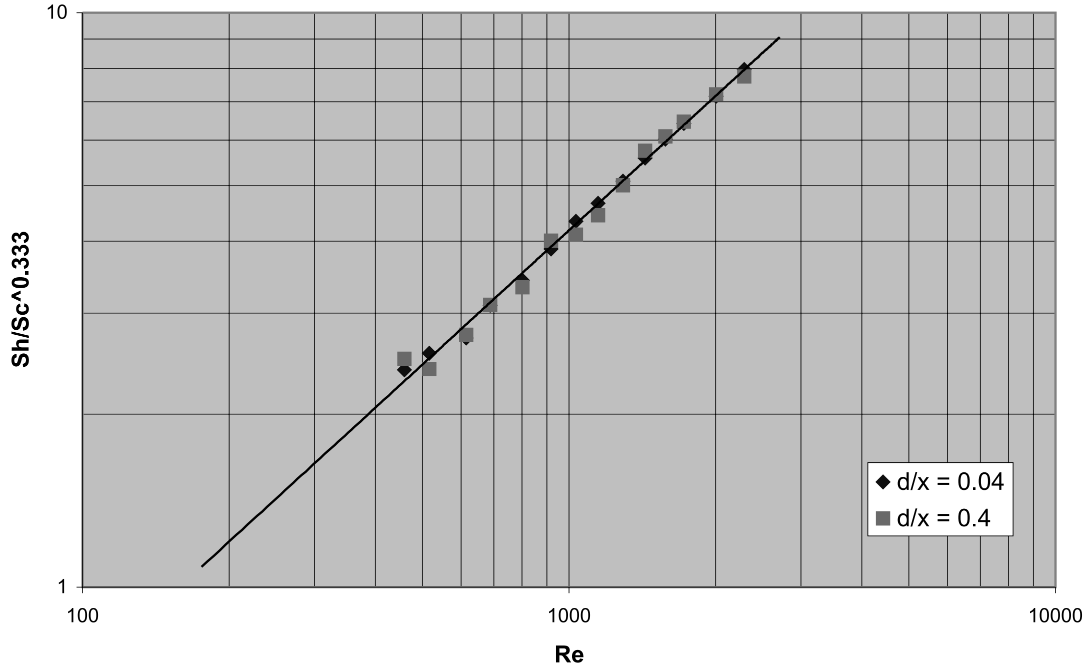

Fig. 4. Pseudo-turbulent correlation for flow along the membrane channels.

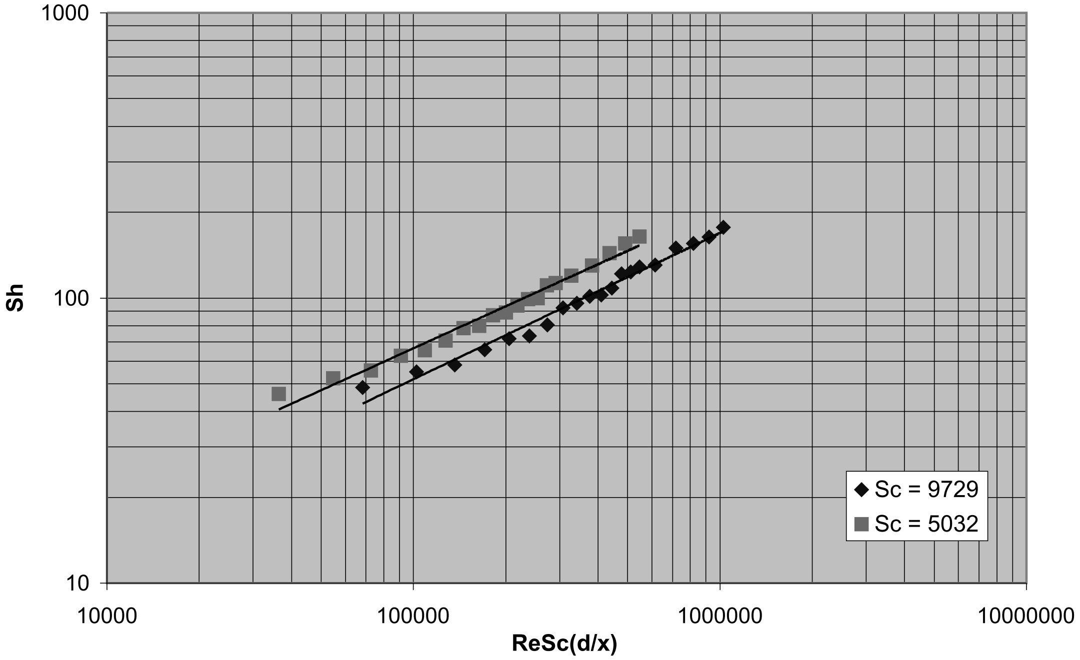

Fig. 5. Effect of viscosity change on mass transfer across membrane channels assuming laminar conditions.

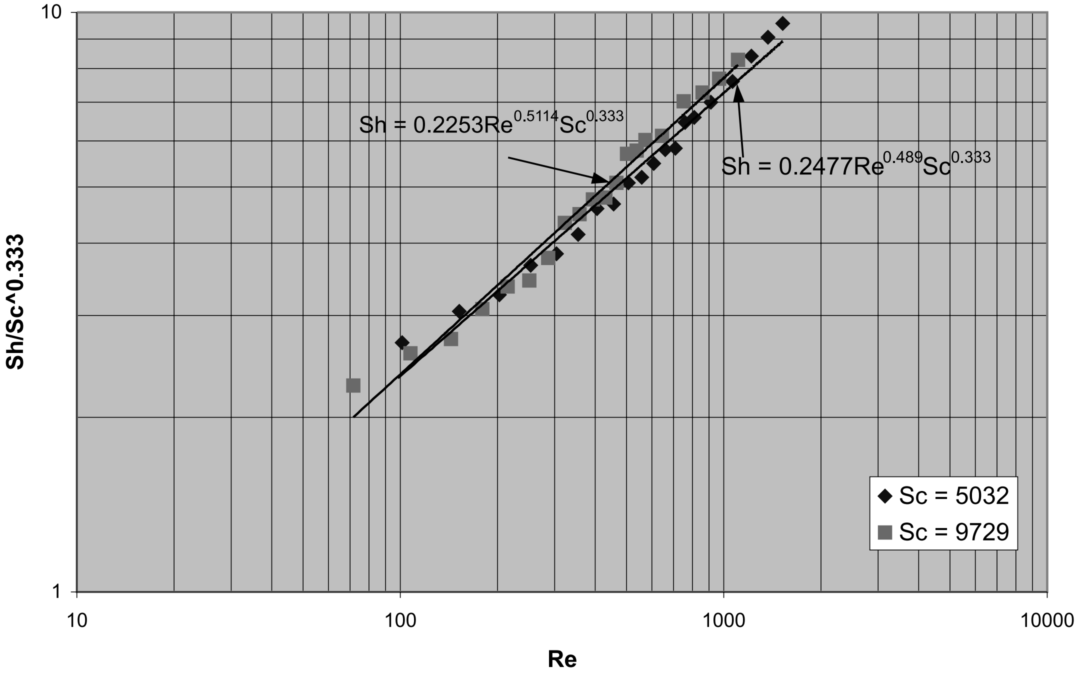

Fig. 6. Effect of viscosity change on mass transfer across membrane channels assuming turbulent condition.

existence of two-dimensional Tollmien–Schlichting (T–S) waves causes a breakdown in the boundary layers thereby promoting turbulence. T–S waves exist in this system due to the higher and lower velocities through the smaller and greater cross-sectional areas, respectively. The effect can be clearly seen as a result of the injection of a dye at the membrane entrance in Fig. 7. Initially the dye flows along the length of the channel,

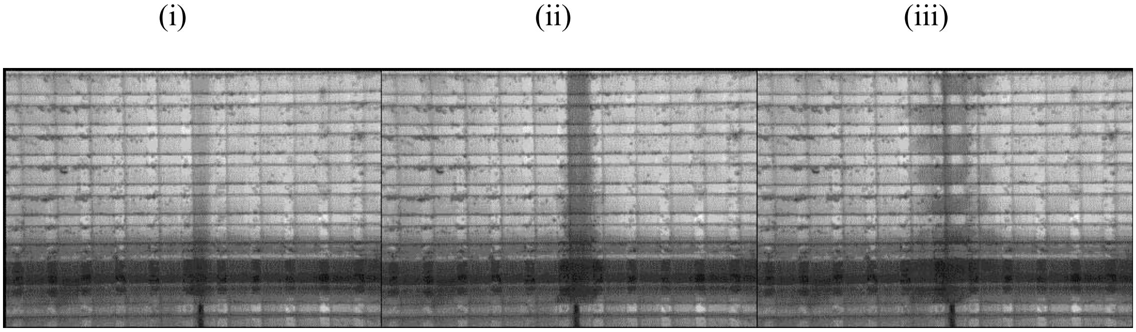

Fig. 7. Effect of T–S waves on mass transfer over corrugated surfaces. (i) Dye injection. (ii) Dye becomes more concentrated in the waves. (iii) Dye disperses tangentially as well as forward.

gradually building in concentration into the T–S waves inside the troughs. Eventually an equilibrium is reached at which point the dye disperses tangentially as well as with the general direction of flow.

4. Conclusions

Mass transport coefficients have been calculated at the surface of two separate cross-corrugated walls along which a liquid will flow under laminar conditions. The mass transfer correlations show that the laminar flow regime expected to exist at low Reynolds Number does not in either case fit the supposition. It is more likely that the irregular flow path caused by the membrane corrugations, resulting in T–S waves, enhances mass transfer to the extent to which turbulent conditions become applicable. The corrugations disturb and destroy the boundary layers, resulting in continuous developing flow along the full length of the reactor, rather than the fully developed flow seen in conventional flat sheet and hollow fibre filtration and reaction units. Visual studies at Newcastle have shown that at low Reynolds numbers, dye injected at the cell entrance mixes effectively within the opening 4–5 mm of the cross-corrugation matrix, a particular characteristic of T–S waves. Further evidence to support the presence of continuous developing flow is given by the independence of mass transfer to the distance from the point of entry, or leading edge, shown in Fig. 4.

Experimental data to support the theory has been obtained from a cross-corrugated polymer film compact heat exchanger by Jachuck and Ramshaw [4], showing significant enhancements in heat transfer performance under laminar flow conditions.

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