Mass transfer enhancement in the membrane aromatic recovery system (MARS): experimental results and comparison with theory

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Abstract

This paper describes an experimental investigation into mass transfer enhancement by chemical reaction in the membrane aromatic recovery system (MARS). The MARS process has recently been commercialised for recovery of cresols from aqueous process streams. In this paper, mass transfer enhancement as a function of the pH and organic concentration of the stripping solution is examined for constant bulk solution conditions. The application of two models of mass transfer enhancement (the Olander and Hatta models) is evaluated by determining the model parameters through independent experiments, limiting cases, and from literature. Model predictions are then compared to experimental data. Three organic compounds are used in this work: phenol, 4-chlorophenol (4CP), and triethylamine (TEA), which span a range of properties of typical molecules recovered by the MARS process. It is concluded that for compounds such as phenol, for which membrane mass transfer resistance dominates the system, there is no reaction enhancement. For compounds such as 4CP and TEA, enhancement effects are important. These were found to be best described through application of the Olander model, which allows for a second-order instantaneous reversible reaction, although the Hatta model, allowing for a second-order instantaneous irreversible reaction, was found to give a good description in some cases as well.
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1. Introduction

Chemical reaction and mass transfer phenomena are often coupled in chemical engineering processes involving multiphase systems (Cussler, 1997). Such processes include gas absorption, extraction, ion exchange and more recently phase transfer catalysis and membrane technology. Chemical reaction can greatly enhance the mass transfer rate, considerably reducing the membrane area required, which usually results in important savings in chemical plant construction. One example of a process where mass transfer phenomena take place accompanied by chemical reaction is the membrane aromatic recovery system (MARS). The MARS is a relatively new process, recently commercialised for industrial wastewater treatment. After successful pilot plant trials

at Solutia, UK (Ferreira et al., 2002a), MARS became operational in industry in December 2002 at Degussa factory, in Knottingley, UK. The MARS process removes dilute organic acids and bases from wastewater streams using a nonporous silicone rubber membrane (permeable to neutral organic compounds, but not to ionic species). The MARS process comprises two stages: in the first, the extraction stage, the neutral organic diffuses from the wastewater solution across the membrane into a stripping solution, where it is converted to its ionic form via an acid/base reaction. For organic bases (for example aniline) the stripping solution is maintained acidic (using HCl) and for organic acids (for example phenol) the stripping solution is maintained alkaline (using NaOH). The acid–base reaction in the stripping solution converts nearly all the unionised organic permeating the membrane into salt form, which does not permeate the membrane. As a result a more concentrated organic solution is produced, which allows for organic recovery by

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neutralization in the second stage of the process. Further description of the MARS technology can be found elsewhere (Han et al., 2001; Ferreira et al., 2002a,b).

Mass-transfer enhancement in the MARS stripping solution takes place due to a reversible second order chemical reaction of the Brönsted acid–base type. These reactions are usually fast enough to be assumed instantaneous, and involve ionic species. The importance of chemical reaction reversibility and ionic mobility (Nernst–Planck effect) were evaluated through a theoretical analysis based on model simulations presented in a previous paper (Ferreira et al., 2004). It was concluded that for typical MARS operating conditions, the Nernst–Planck effect is not important and can be neglected. According to that theoretical analysis, accurate mathematical description of the mass transfer phenomena in MARS can be achieved using models proposed by Olander (Olander, 1960) and Hatta (Hatta, 1928, 1932). These models revealed that there is an important effect of pH and total organic concentration in the stripping solution on mass transfer, which can be explained by the coupling of chemical reaction and mass transfer.

In industrial MARS applications the wastewater concentration is a variable along the membrane tube lumen or over time in the extraction tank, respectively, for continuous or batch operations (Ferreira et al., 2004). However, the foregoing models calculate the chemical reaction mass transfer enhancement for fixed bulk solution concentrations. Hence, in this work, laboratory experiments to investigate model predictions were designed to be under steady-state conditions at fixed concentrations in the wastewater and stripping solution.

The purpose of this paper is, firstly, to investigate experimentally the effect of chemical reaction on mass transfer. Secondly, the ability to describe the overall mass flux using the foregoing models, coupling chemical reaction and diffusion, will be evaluated. Parameters for the models were determined from independent experiments and used to describe the mass transfer.

2. Mathematical models

2.1. Models overview

The Hatta and Olander models describe mass transfer enhancement effect using different assumptions. The Hatta model assumes that the reaction is irreversible and that all the neutral organic is consumed at the reaction plane located within the stripping solution liquid film, and so the neutral organic concentration in the bulk stripping solution is zero. In the Olander model, chemical reaction reversibility governed by an equilibrium constant is assumed across the stripping solution liquid film, and therefore this model allows for the existence of neutral organic concentrations in the bulk stripping solution. While the Olander model is closer to reality in its assumptions, the Hatta model requires

less parameters, since it does not need information about the equilibrium constant, ionic product diffusion coefficient or stripping solution organic concentrations. Therefore it is useful to identify organic compounds and conditions under which the Hatta model can be used to accurately predict mass transfer flux. Such conditions are mainly related to pH and organic concentrations in the stripping solution, and to the equilibrium constant of the organic under consideration. The higher the equilibrium constant, the less important the reversibility of the chemical reaction, and the closer the Olander and Hatta model solutions approach each other (Ferreira et al., 2004). Another important parameter, which should also be considered, is the organic permeability through the membrane, which determines the relative liquid film resistance contribution to the overall resistance. A summary of the basic ideas of the two models is presented in Fig. 1.

2.2. Model equations

Mathematical derivation of the models used can be found in a previous paper (Ferreira et al., 2004), and are summarised in this section.

An organic flux equation, based on concentration driving force is used in these models (Eq. (1)).

$$J_{ov} = I_m K_{ov} (A_{f,b} - A_{s,b}). \tag{1}$$

The overall mass transfer coefficient is defined in Eq. (2) using the resistances in series approach, as a function of enhancement factor (E), stripping solution liquid film mass transfer coefficient (k_s) and a "grouped" mass transfer coefficient (k_g) that includes feed solution liquid film and membrane mass transfer coefficients:

$$\frac{1}{K_{ov}} = \frac{1}{k_g} + \frac{1}{E k_s} \quad \text{with} \quad \frac{1}{k_g} = \frac{1}{k_f} + \frac{1}{k_m}. \tag{2}$$

Hatta and Olander models have different calculated enhancement factors given by, respectively, Eqs. (3) and (4)

$$E = 1 + \frac{D_B}{D_A} \frac{B_{s,b}}{A_{s,i}}, \tag{3}$$

$$E = 1 + \frac{D_{AB}}{D_A} \frac{K B_{s,b}}{1 + \frac{D_{AB}}{D_B} K A_{s,i}}. \tag{4}$$

The enhancement factor is dependent on the (non-measurable) neutral organic concentration at the membrane/stripping solution interface $A_{s,i}$. For the Hatta model, in principle Eq. (5) can be used to calculate $A_{s,i}$, in the case when the chemical reaction front does not reach the membrane/stripping solution interface, however, Eq. (6) is preferable since it gives a more useful prediction for the flux enhancement.

$$A_{s,i} = \frac{(k_g/k_s)A_{f,b} - (D_B/D_A)B_{s,b}}{(1 + k_g/k_s)} \quad \text{for } A_{s,i} > 0, \tag{5}$$

$$\frac{J_{ov}}{J_{ov}^0} = \frac{K_{ov}}{K_{ov}^0} = 1 + \frac{D_B}{D_A} \frac{B_{s,b}}{A_{f,b}} \quad \text{for } K_{ov} < k_g. \tag{6}$$
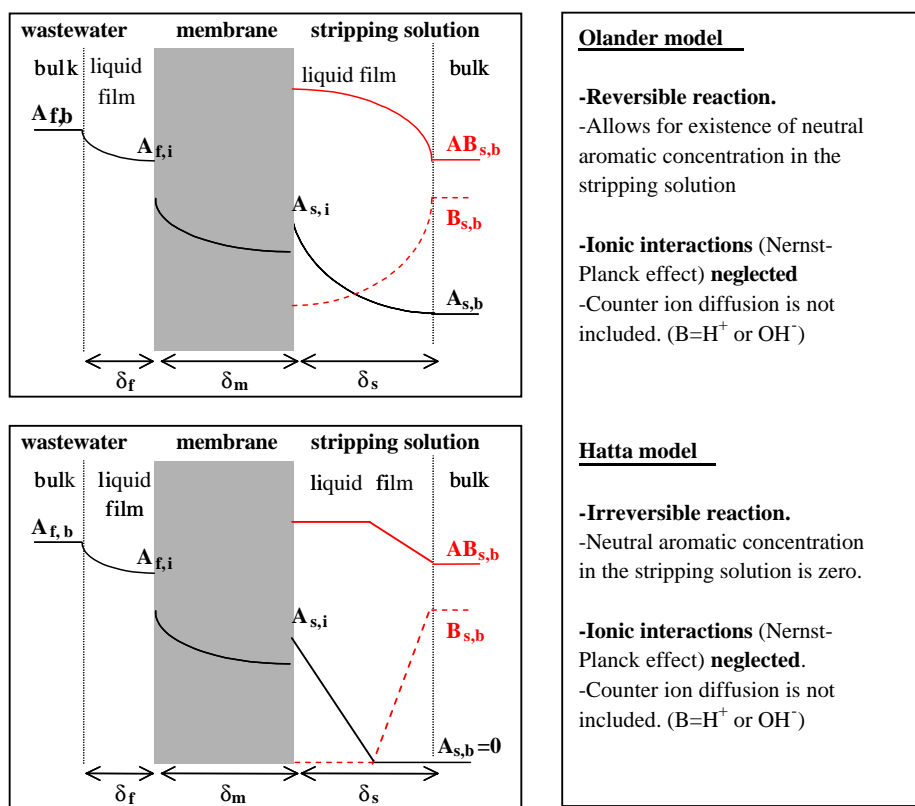
Fig. 1. Schematic representation of concentration profiles in the Hatta and Olander models.

For the Olander model an analytical solution was developed (Ferreira et al., 2004), and $A_{s,i}$ can be calculated from Eq. (7), on the basis of model input parameters and variables

$$A_{s,i} = \frac{-b + \sqrt{b^2 - 4ac}}{2a},$$ (7)

where

$$a = \left(1 + \frac{k_g}{k_s}\right) \frac{D_{AB}}{D_B} K,$$

$$b = \left(1 + \frac{k_g}{k_s}\right) + \frac{D_{AB}}{D_A} K B_{s,b}$$
$$- \left(A_{s,b} + \frac{k_g}{k_s} A_{f,b}\right) \frac{D_{AB}}{D_B} K,$$

$$c = -\left[\frac{k_g}{k_s} A_{f,b} + A_{s,b}\left(1 + \frac{D_{AB}}{D_A} K B_{s,b}\right)\right].$$

2.3. Model input parameters

The model input parameters are categorised into three groups: (i) operating parameters; (ii) mass transfer properties, and; (iii) chemical compound properties.

The operating parameters group (i) includes: the concentration of ionic reagent (NaOH or HCl), added to control the stripping solution pH (C^{add}); the feed bulk concentration

($A_{f,b}$); and the stripping solution pH. Additionally, three intrinsic system variables are also defined:

(a) The total organic concentration in the stripping solution bulk ($C_{s,b}^T$), which at steady state is controlled by the concentration of ionic reagent (C^{add}) as expressed in Eq. (8) (Ferreira et al., 2002b)

$$C_{s,b}^T(M) = \frac{1}{\frac{\rho^{add}}{\rho_s} \frac{1}{C^{add}(M)} + \frac{M w_A}{1000 \rho_s}}.$$ (8)

(b) The free ionic reagent concentration ($B_{s,b}$), which is a function of the stripping solution pH, and can be calculated from Eq. (9), for extraction of organic acid or base, respectively;

$$B_{s,b} = \frac{10^{pH}}{K_w} = 10^{pH-14} \quad \text{and} \quad B_{s,b} = 10^{-pH}.$$ (9)

(c) The neutral organic concentration in the stripping solution bulk ($A_{s,b}$), which is calculated from Eq. (10) (Ferreira et al., 2002b), as a function of the stripping solution pH (throughout $B_{s,b}$), the equilibrium constant (K), and the total organic concentration in the stripping solution bulk ($C_{s,b}^T$). Consequently, for a stripping solution at steady state and constant pH, $A_{s,b}$ is also a constant over time.

$$A_{s,b} = \frac{C_{s,b}^T}{1 + K B_{s,b}}.$$ (10)

Table 1
Experimental conditions, solutions and chemical compound properties, and model parameters

Compound	Phenol	TEA	4CP
Flow—pump A $(L\,s^{-1})$	4.2×10^{-6}	12.7×10^{-6}	13.1×10^{-6}
Membrane length (m)	0.92	0.92	5
Membrane area (m^2)	8.7×10^{-3}	8.7×10^{-3}	47.1×10^{-3}
Temperature ($^\circ$C)	50	30	30
C^{add} (M):NaOH/HCl	2.75	2.74	6.15
$C_{s,b}^T$ (M)	2.23	2.36	3.81
ρ^{add} $(kg\,L^{-1})$	1.10	1.00	1.23
ρ_s $(kg\,L^{-1})$	1.10	1.10	1.25
μ_s (cP)	1.9	2.9	7.3
CMC (wt%)	0.97	1.00	2.58
$Mw_A (g\,mol^{-1})$	94	101	128.5
pKa @25°C	10	10.7	9.18
K (M^{-1})	10^4	5×10^{10}	7×10^4
D_A $(m^2\,s^{-1})$	8.9×10^{-10}	7.0×10^{-10}	9.4×10^{-10}
D_{AB} $(m^2\,s^{-1})$	8.6×10^{-10}	7.5×10^{-10}	9.7×10^{-10}
D_B $(m^2\,s^{-1})$: B$=$H$^+$, OH$^-$	5.3×10^{-9}	9.3×10^{-9}	5.3×10^{-9}

The mass transfer properties group (ii) includes k_g and k_s, which will be evaluated in the Results and discussion section.

Finally, the chemical compound properties group (iii) includes input parameters whose values can be found in the literature: molecular weights (Lide, 1995); the aqueous diffusion coefficients (Leaist and Lu, 1997; Saterlay and Foord, 2001; Washburn, 2003) and the equilibrium constants (K). The equilibrium constant is directly related to the acid dissociation constant K_a. For organic bases or acids respectively:

$$K = \frac{AB}{A\,B} = \frac{1}{K_a} \quad \text{or} \quad K = \frac{AB}{A\,B} = \frac{1}{K_b} = \frac{K_a}{K_w}. \tag{11}$$

Note that these literature parameters are actually for solutions at infinite dilution, and are usually recorded at room temperature. However, it is assumed here that temperature, viscosity, ionic strength and other effects resulting from deviations from ideal behaviour will affect all diffusion coefficients equally, and since the diffusion coefficients are included in the model as ratios (Eqs. (3) and (4)), this effect will be negligible. The equilibrium constant is a key parameter for the Olander model because it has an effect on both terms of Eq. (1), by means of the enhancement factor E (Eq. (4)) and the concentration of neutral organic in the stripping solution bulk $A_{s,b}$ (Eq. (10)). Therefore experimental measurements of $A_{s,b}$ were performed for the operational pH values, and the experimentally estimated equilibrium constant values compared with the theoretical ones predicted from literature pK_a values. A summary of the model input parameters values used in this study is presented in Table 1.

3. Experimental

3.1. Choice of chemical compounds and experimental conditions

Three model compounds are considered in this paper: phenol, triethylamine (TEA) and 4-chlorophenol (4CP). Permeabilities (Han et al., 2001; Ferreira et al., 2002b) and organic acid dissociation constants (Lide, 1995) found in the literature are presented in Table 1.

Phenol is a typical toxic organic acid that can be recovered from industrial wastewaters by MARS, and is also the compound on which most MARS studies have been performed (Han et al., 2001; Ferreira et al., 2002a). It has an intermediate equilibrium constant value, $10^4\,M^{-1}$, implying that, within the MARS stripping solution pH range, chemical reaction reversibility can be important in determining mass transfer rates.

TEA is an organic base, which can react with hydrochloric acid to form triethylammonium chloride. Membrane permeability to TEA is high (about eight times the phenol permeability) (Han et al., 2001; Ferreira et al., 2002b) and therefore in MARS applications the stripping solution liquid film resistance makes a major contribution to the overall mass transfer resistance, making TEA an interesting compound for chemical reaction mass transfer enhancement studies. Moreover, the acid–base equilibrium constant of TEA is high at $5 \times 10^{10}\,M^{-1}$. Therefore at the operating pH values, the concentration of neutral TEA in the stripping solution is virtually zero. Theoretically, in this scenario, the Hatta and Olander models give identical predictions and the mass transfer enhancement can be calculated assuming that the reaction is irreversible (Ferreira et al., 2004).

A third compound, an organic acid, 4-chlorophenol (4CP) was chosen. 4CP has membrane permeability about twice that of phenol (Han et al., 2001) and also an intermediate equilibrium constant, $7 \times 10^4\,M^{-1}$. Therefore, for a stripping solution pH at which the concentration of neutral organic in the bulk stripping solution is significant, it is expected that the chemical reaction reversibility will play an important role in the mass transfer enhancement. Thus the experimental conditions have been chosen in such a way as to test the Hatta and Olander models under conditions where their predictions for the mass transfer enhancement differ.

3.2. Chemicals, membrane and analytical techniques

Dichloromethane (DCM), carboxymethyl cellulose (sodium salt) ultra-low viscosity (CMC), 4CP and TEA were obtained from Aldrich-Sigma as pure chemicals. Solid phenol, hydrochloric acid 37 wt% (~12 M), and solid sodium hydroxide pellets were, respectively, obtained from Lancaster UK and Merck UK. All solutions were prepared using deionised water.

All samples were diluted with deionised water and the pH of the resulting solution was adjusted in order to ensure that the organic is in its neutral form (pH = 3 for phenols and 13 for TEA). 0.5 mL of this solution was extracted with 1 mL of DCM and 1 μL of the extracting DCM solution injected in a gas chromatograph (Agilent 6850) fitted with a megabore column HP1 30 m × 0.32 mm × 0.25 μm, and FID detector. Helium was used as a carrier gas. For all three compounds, the coefficient of variation for these assays (over 5 measurements) was lower then 5% at 0.01 M and the detection limit was established at 10^{-5} M.

The membrane tube (Silex Ltd, UK) used in this study has an internal diameter of 3 mm and a wall thickness of 0.5 mm. Membrane tube lengths used in each of the experiments are shown in Table 1. The membrane material is a cross linked 70 wt% polydimethylsiloxane polymer with 30 wt% silica dioxide as a filler.

3.3. Experimental apparatus

Figs. 2 and 3 show, respectively, experimental set-ups I and II, in which four different types of experiments were performed: (i) Mass-transfer experiments without chemical reaction; (ii) k_g measurement experiments; (iii) equilibrium experiments; and (iv) mass transfer experiments with chemical reaction.

Pump A flow rates (F_f) used for each of the three model compounds, and shown in Table 1, were chosen according to the expected organic flux across the membrane, in order to provide a measurable concentration difference between the inlet and the outlet (overflow) of the feed solution. In both experimental set-ups, the feed solution was circulated by pump B with a constant flow rate of 6.7×10^{-3} L s^{-1} in all the experiments, corresponding to a Reynolds number of 2830 inside the membrane tube lumen, and to a residence time in the feed tank of 60 s.

3.3.1. Experimental set-up I

Experimental set-up I, shown in Fig. 2, was used for phenol extraction. This set-up includes a 1 m long tubular mass exchanger with an internal diameter of 10 mm. The tubular membrane was positioned coaxially inside the exchanger. Pump C, with a flow rate of 2.7×10^{-4} L s^{-1}, gave a Reynolds number of 18 on the shell side, for a measured stripping solution viscosity of 1.9 cP. The lower the flow rate of the stripping solution, the higher is the stripping solution liquid film resistance, and so the greater the effect of

chemical reaction enhancement on the mass transfer. However, as phenol is extracted, it reacts with the available free hydroxide, and this can cause an axial pH drop along the shell side of the mass exchanger, accompanied by an increase of the phenol concentration. As explained earlier, in this work we want to minimize any variations in bulk liquid concentrations, and therefore pump C flow rate has to be sufficient, compared with the phenol flux through the membrane, to ensure that the axial phenol concentration increase and pH drop are negligible. It is desirable to deliberately operate with a high stripping solution film resistances, so as to better reveal the effects of chemical reaction enhancement. However, high stripping solution liquid film resistance and negligible axial concentration gradients required opposing flow rates for pump C and so were impossible to achieve in the same set-up for TEA and 4CP, which have a higher membrane permeability and organic flux through the membrane compared to phenol. Hence, extractions of 4CP and TEA were performed in experimental set-up II, shown in Fig. 3. In experimental set-up I, all the vessels and the mass exchanger were immersed in a water bath at 50 °C.

3.3.2. Experimental set-up II

In this set-up the membrane tube coil was immersed into a 5 L stripping solution vessel, making it difficult to define a Reynolds number at the membrane shell side. The stripping solution hydrodynamic conditions were determined by the mixing provided by the magnetic stirrer and by the pump D flow rate (pump D was set to provide a residence time in the stripping solution tank of 900 s in both set-ups), which were kept constant in all experiments to ensure data consistency. In experimental set-up II, the temperatures of the feed and stripping solutions were kept constant at 30 °C by a feed back loop connected to the magnetic stirrer hot plates.

3.3.3. Stripping solution

The stripping solution (S) used in this study was similar to the one used for industrial MARS applications, with total organic concentration ($C_{s,b}^T$) high enough to allow for organic recovery by neutralisation. The stripping solution pH was maintained at steady state by a feedback loop, with a pH probe immersed in the solution and a pump adding ionic reagent solution (C^{add}) as required to maintain pH at a constant value. The stripping solution pH was acidic for TEA extraction maintained by adding hydrochloric acid (2.74 M HCl) solution, and alkaline for phenol and 4CP extraction, maintained by adding sodium hydroxide (2.75 or 6.15 M NaOH, respectively) solution. The stripping solution volume was kept constant by an overflow from the stripping solution vessel. At steady state, the moles of organic collected in the overflow are equal to the moles of organic extracted from the feed solution, and the total organic stripping solution concentration ($C_{s,b}^T$) remains constant over time at a value calculated from Eq. (8) on the basis of $C^{add} C_{s,b}^T$ and C^{add}. Values used for each experiment are shown in Table 1.
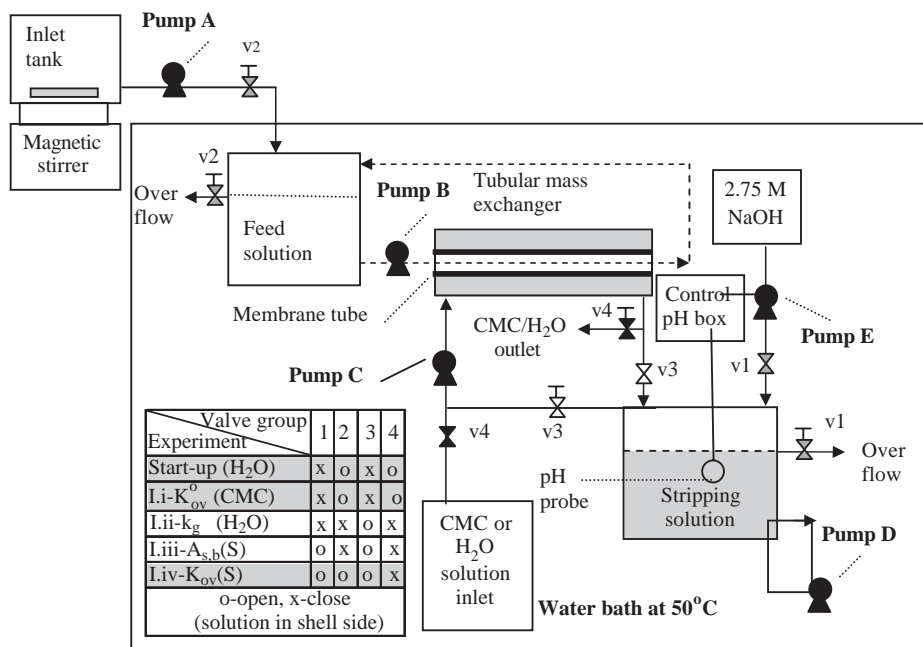
Fig. 2. Schematic diagram of experimental set-up I for phenol extraction, including valve group positions for experiments—i–iv. (Experiments marked in grey in the table were continuous with respect to the feed solution.)
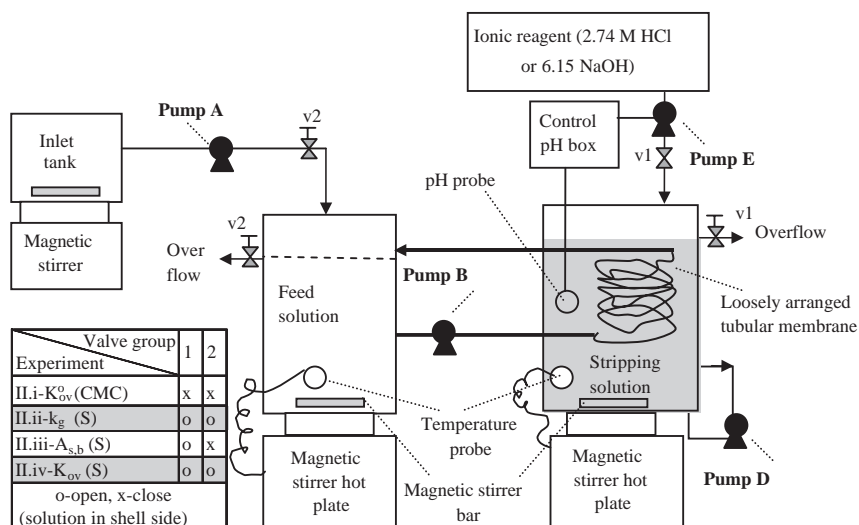

Fig. 3. Schematic diagram of experimental set-up II for TEA and 4CP extraction, including valve group positions for experiments—i–iv. (Experiments marked in grey in the table were continuous with respect to the feed solution.)

3.4. Experimental strategy

The general strategy below was followed for experiments in this work:

1. Determination of the model input parameters from independent set of experiments;
2. Theoretical mass transfer enhancement calculations based on the above parameters, and choice of experimental conditions, where the chemical reaction mass transfer enhancement can be clearly revealed;

3. Experimental determination of the mass transfer enhancement for comparison to predicted values.

3.4.1. Experiment (i)—mass transfer without chemical reaction: measurement of K_{ov}^0

To evaluate the overall mass transfer coefficient (K_{ov}^0) without chemical reaction, the stripping solution was replaced by a nonreactive solution, maintaining the same hydrodynamic conditions. The stripping solution is viscous compared with water, and the viscosity has a significant effect on the liquid film resistance (Cussler, 1997). Hence,

carboxymethyl cellulose (CMC) was used as a viscosity enhancer to simulate stripping solution viscosity. The viscosity of the stripping solutions, and the concentrations of the corresponding CMC aqueous solutions used, are given in Table 1. Calibrations for viscosity of CMC solution concentrations are presented in Fig. 8 in the Appendix.

Experiments to measure phenol K_{ov}^0 were run in a continuous mode, with valve groups 3 and 4 in set-up I in "off" and "on" positions, respectively. The experiment was started up by feeding single pass mode distilled water (pH 3, adjusted with HCl) solution to the shell side of the tubular mass exchanger. Once the system was stable, a CMC solution was fed to the shell side of the mass exchanger in a single pass mode. Pump C flow rate was high enough to ensure that the phenol concentration in the CMC solution $A_{s,b}$ can be assumed equal to zero in Eq. (12), which represents the process mass balance

$$K_{ov} = \frac{F_f}{I_m} \frac{(A_{in} - A_{f,b})}{(A_{f,b} - A_{s,b})}. \tag{12}$$

This assumption was confirmed by measuring phenol concentrations in the mass exchanger outlet CMC solution.

Experiments for K_{ov}^0 measurements of TEA and 4CP were run in a batch mode in set-up II, with the MARS stripping solution replaced by an appropriate CMC solution and valve groups 1 and 2 closed. K_{ov}^0 was estimated separately from Eq. (13) for the feed solution side, and from Eq. (14) for the CMC solution side.

$$\ln \left[\frac{A_{f,b}(t)}{A_{f,b}(t=0)} \left(1 + \frac{V_f}{V_s} \right) - \frac{V_f}{V_s} \right]$$
$$= - \left(\frac{1}{V_f} + \frac{1}{V_s} \right) K_{ov} I_m t, \tag{13}$$

$$\ln \left[1 - \frac{A_{s,b}(t)}{A_{f,b}(t=0)} \left(1 + \frac{V_s}{V_f} \right) \right]$$
$$= - \left(\frac{1}{V_f} + \frac{1}{V_s} \right) K_{ov} I_m t. \tag{14}$$

The final K_{ov}^0 value in this case was taken as an average of these two values.

3.4.2. Experiment (ii)—k_g measurement

Chemical reaction enhancement is at a maximum when the stripping solution liquid film resistance is completely eliminated. After this point, increasing the stripping solution ionic reagent concentration ($B_{s,b}$) no longer increases mass transfer flux. The experimental value for the overall mass transfer coefficient measured under these conditions is due entirely to the feed solution liquid film and the membrane mass transfer resistances, and was taken as k_g. This approach was used for k_g estimation for TEA and 4CP. However, due to the high K_a value of phenol, the MARS system operates at the limiting pH for the membrane material chemical resistance and so this approach was not practical. For phenol extraction, this parameter was measured

in an independent batch experiment. Valve groups 1 and 2 in set-up I were closed, the MARS stripping solution in the tank (see Fig. 2) was replaced by water, and the pump C flow rate was increased to a value of $3.3 \times 10^{-2} \, L \, s^{-1}$, corresponding to a Reynolds number of 4244, which should be high enough to eliminate the liquid film resistance (Oliveira et al., 2001). Eqs. (13) and (14) were used to estimate the mass transfer coefficient K_{ov}, which is equal to k_g under these conditions.

3.4.3. Experiment (iii)—equilibrium measurement of $A_{s,b}$

The neutral organic concentration in the stripping solution bulk ($A_{s,b}$) can be calculated using Eqs. (10) and (11), on the basis of pK_a found in the literature for dilute solutions at room temperature. However, the stripping solution is highly concentrated in organic salt (typical values higher than 2 M phenol or TEA salts) and so deviation from dilute solution ideal behaviour is expected. Moreover, phenol experiments were done at 50 °C, and 4CP and TEA extractions were performed at 30 °C. Therefore to test the accuracy of the theoretically calculated values, $A_{s,b}$ was estimated experimentally at different pH values for the range of stripping solution total organic concentrations ($C_{s,b}^T$) used in this work.

The experiments were conducted as follows: the valve group 2 in set-ups I and II were closed and the organic concentration in the feed solution allowed to decrease to a constant value. At this point there is no chemical potential gradient between the feed and stripping solutions, which in the absence of a pressure driving force implies that the activities of the unionised organic on both sides of the membrane are equal. Given that the feed solution is dilute enough to be assumed ideal, the measured feed solution organic concentration at the chemical potential equilibrium was taken as equal to $A_{s,b}$. The experimental equilibrium constant (K^{exp}) value then can be estimated from Eq. (10) based on the experimentally measured $A_{s,b}$ values at the respective stripping solution pH (i.e., $B_{s,b}$) and total organic concentration ($C_{s,b}^T$).

3.4.4. Experiment (iv)—mass transfer with chemical reaction: measurement of K_{ov}

Measurements of the overall mass transfer coefficient (K_{ov}) with chemical reaction were performed at steady state. It is important that all the bulk concentrations are constant over time, since the chemical reaction enhancement predicted by the models depends on these concentrations. Pump flows and stirrer speeds were maintained equal to those used in experiment (i) to maintain the same hydrodynamic conditions. The membrane material is impermeable to ionic compounds. Therefore, to ensure that the organic compound on the feed side of the membrane is completely in neutral form, the pH of the feed solution was adjusted to a value of 3 for phenol or 4CP extraction, and 13 for TEA extraction using, respectively, hydrochloric acid and sodium

hydroxide. At steady-state K_{ov} can be calculated from Eq. (12), taking into account the neutral organic concentration $A_{s,b}$ measured in experiment (iii).

4. Results and discussion

Note that henceforth, for clarity, the experiments will be denoted by two numbers—firstly the number of the set-up used, and secondly the number describing the type of the experiment, i.e.,—I.i.—experiment performed in set-up I, of experimental type i.

4.1. Phenol extraction

Phenol experiments were performed using experimental set-up I as shown in Fig. 2, as described in the Experimental section, and the results are presented in Fig. 4.

4.1.1. Model input parameters and model predictions

The overall mass transfer coefficient without chemical reaction (K_{ov}^0) was determined in a continuous experiment (I.i). A 0.97 wt% CMC solution at pH 3 was used to simulate the MARS stripping solution viscosity. An average value of $(1.7 \pm 0.2) \times 10^{-7}\,\mathrm{m\,s^{-1}}$ was estimated from Eq. (12), assuming $A_{s,b} = 0$.

k_g was estimated from Eqs. (13) and (14) as $(2.1 \pm 0.3) \times 10^{-7}\,\mathrm{m\,s^{-1}}$, an average value of three measurements obtained in a batch experiment (I.ii). Thus the ratio $k_g/K_{ov}^0 = 1.2$ corresponds to the maximum mass transfer enhancement predicted for this system, which occurs when the stripping solution liquid film mass transfer resistance is completely eliminated. It is expected that experimental measurement of such a small difference may be difficult.

A theoretical stripping solution liquid film mass transfer coefficient (k_s) in the absence of chemical reaction, was then calculated at a value of $1.0 \times 10^{-6}\,\mathrm{m\,s^{-1}}$, using the above k_g and K_{ov}^0 values and applying the resistances in series approach (Eq. (2)).

Using the estimated values of k_g and k_s, and the input values listed in Table 1 a stripping solution pH (as $B_{s,b}$) can be calculated, above which maximum mass transfer enhancement is predicted, i.e., $K_{ov} = k_g$. For the Hatta model, this value was calculated directly from Eq. (6). For the Olander model this pH was estimated from Eq. (2), by substituting the corresponding enhancement factor (Eq. (4)) and interfacial concentration (Eq. (7)), and solving the final equation for the case where $K_{ov} = 0.99\,k_g$. For a 0.40 M phenol feed concentration ($A_{f,b}$), the Hatta and Olander models predict maximum mass transfer enhancement by the acid–base chemical reaction at stripping solution pH values of, respectively, 12.2 and 12.9, corresponding to hydroxide concentrations ($B_{s,b}$) of 0.02 and 0.08 M.

In the equilibrium experiment (I.iii), the phenol feed concentration decreases over time until it reaches an equilibrium value of 3.9×10^{-3} M. This value should be equal to
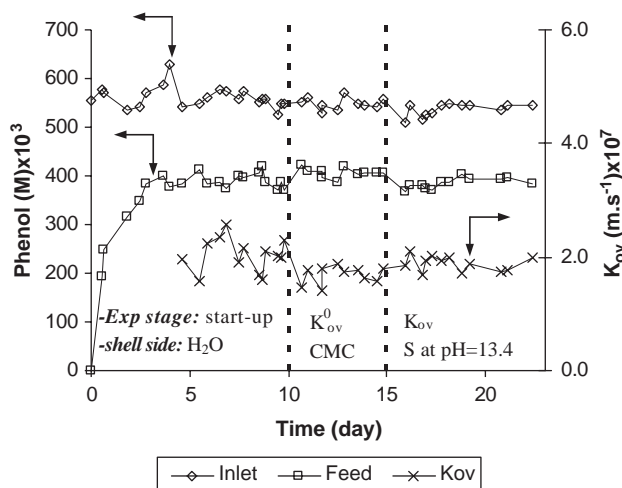

Fig. 4. Experimental results for continuous phenol extraction with and without chemical reaction, including inlet and feed solution phenol concentrations and the estimated overall mass transfer coefficients.

the neutral phenol concentration ($A_{s,b}$) in the stripping solution with total phenol concentration ($C_{s,b}^T$) of 2.23 M at pH 13.4 ($B_{s,b} = 0.25$ M). This experimental value is in marked variance with the theoretical value of 0.9×10^{-3} M, calculated from Eq. (10) using the theoretical equilibrium constant based on pK_a at room temperature (Table 1).

By substituting the measured value for $A_{s,b}$, into Eq. (10), a new value of $2 \times 10^3\,\mathrm{M^{-1}}$ was estimated for the experimental equilibrium constant (K), which is an order of magnitude lower than the theoretical one ($10^4\,\mathrm{M^{-1}}$). Such differences in the K values can probably be attributed to the experimental temperature used (50 °C), which is consistent with the exothermic nature of the chemical reaction; and to deviations from ideal behaviour of the stripping solution, which has high total phenol concentration (2.23 M) and ionic strength (about 4.50 M). Evidence that such systems tend to exhibit a non-ideal behaviour can be found elsewhere (Cocchini et al., 1999; Han et al., 2001). Although negligible compared with the bulk feed solution concentration (0.40 M, Fig. 4) the measured concentration of $A_{s,b}$ was still taken into account in the mass transfer coefficients calculations (Eq. (12)).

Using the equilibrium constant value experimentally estimated, the stripping solution pH sufficient for maximum enhancement for a 0.40 M phenol feed solution was recalculated from the Olander model at a value of 13.2. Therefore a stripping solution pH value of 13.4, corresponding to a hydroxide concentration of 0.25 M, was employed in the experiment with chemical reaction. This value is well above the predicted values, ensuring that the experiment was performed in the maximum mass transfer enhancement regime.

Thus for a stripping solution with a flow rate of $2.7 \times 10^{-4}\,\mathrm{L\,s^{-1}}$ at maximum enhancement, a total phenol concentration increase of 3×10^{-3} M was calculated along the shell side of the tubular mass exchanger. This value was obtained from Eq. (1) using I_m, k_g, $A_{f,b}$ and $A_{s,b}$ values of

$0.0087 \, \text{m}^2$, $2.1 \times 10^{-7} \, \text{m s}^{-1}$, $0.40 \, \text{M}$ and 0, respectively. This value is negligible compared with the $2.23 \, \text{M}$ total phenol concentration in the stripping solution and can be calculated to result in a hydroxide concentration drop from 0.250 to $0.247 \, \text{M}$ along the shell side of the membrane, corresponding to a negligible pH drop of 0.01 units. Therefore it can be concluded that there is no significant axial pH or phenol concentration gradient, and the stripping solution at the membrane shell side can be assumed homogeneous.

4.1.2. Mass transfer measurements with chemical reaction

The experimental results for phenol extraction with chemical reaction are shown in Fig. 4. Experiment (I.iv) for K_{ov} measurements was performed using a typical MARS stripping solution (S) at steady state. This solution has a total phenol concentration of $2.23 \, \text{M}$ and was recirculated between the shell side of the mass exchanger and the stripping vessel. A $2.75 \, \text{M}$ NaOH solution was used to control pH at a value of 13.4. The flow rate of pump C was kept the same as in the K_{ov}^0 measurements, i.e., experiment without chemical reaction (I.i), and it is a fair assumption that since the hydrodynamic conditions on the shell side of the membrane were equal for both experiments, the differences in mass transfer coefficients should reflect the chemical reaction effect only.

According to the model predictions, at the experimental conditions used, the introduction of chemical reaction should lead to a maximum of 1.2 times increase in the overall phenol mass transfer coefficient; from an input value of $1.7 \times 10^{-7} \, \text{m s}^{-1}$ for mass transfer coefficient in the absence of chemical reaction (K_{ov}^0) to a value of $2.1 \times 10^{-7} \, \text{m s}^{-1}$ for k_g at maximum chemical reaction enhancement, expected at a stripping solution pH value of 13.4. The measured average K_{ov} value of $(1.9 \pm 0.1) \times 10^{-7} \, \text{m s}^{-1}$ obtained in experiment (I.iv) for the overall phenol mass transfer coefficient with chemical reaction (K_{ov}), is indeed slightly higher than the K_{ov}^0 average value of $(1.7 \pm 0.2) \times 10^{-7} \, \text{m s}^{-1}$ measured in experiment (I.i) in the absence of chemical reaction, corroborating that the chemical reaction is responsible for the mass transfer enhancement. However, the mass transfer coefficient measured with chemical reaction is slightly lower than k_g, suggesting that, contrary to the model predictions, the mass transfer enhancement is not at a maximum at pH 13.4. Essentially, the measured values are so close and within the experimental error that is difficult to draw any definitive conclusion about the chemical reaction mass transfer enhancement. The small differences between mass transfer coefficients with and without chemical reaction imply that the membrane is actually the main phenol mass transfer resistance in this system.

4.2. Triethylamine extraction

Triethylamine (TEA) is an organic base, hence the stripping solution used in the MARS extraction was an acidic solution maintained at a steady-state total TEA concentration of $2.36 \, \text{M}$ by addition of $2.74 \, \text{M}$ HCl to control pH at a constant value. As already mentioned, TEA was chosen as a model compound because of its high membrane permeability, which ensures a significant contribution of the stripping solution liquid film resistance to the overall mass transfer resistance, making the effect of chemical reaction enhancements on the mass transfer coefficient more significant than for phenol.

4.2.1. Model input parameters and model predictions

The overall mass transfer coefficient without chemical reaction (K_{ov}^0) was measured in a batch experiment (II.i). In this experiment, the stripping solution (see Fig. 3) was replaced with a solution of $1 \, \text{wt}\%$ CMC, adjusted to pH 13. K_{ov}^0 was estimated using Eqs. (13) and (14) as $(0.93 \pm 0.03) \times 10^{-6} \, \text{m s}^{-1}$, an average value of two independent measurements.

The k_g value used as an input for the TEA model simulations corresponds to the maximum measured value of overall mass transfer coefficient, $1.52 \times 10^{-6} \, \text{m s}^{-1}$, obtained from experiment (II.ii), for k_g measurements (see Table 2). This value was taken when the measured overall mass transfer coefficient did not increase further as $B_{s,b}$ increased (i.e., the stripping solution pH decreased) and therefore it can be assumed that the stripping solution liquid film resistance was completely eliminated and K_{ov} equals k_g. As shown in Table 3, such conditions are observed for stripping solution pH below 2, at a feed concentration of $40 \times 10^{-3} \, \text{M}$ TEA. Thus the maximum possible mass transfer enhancement for this system is $k_g/K_{ov}^0 = 1.63$. This enhancement is considerably higher than the one for the phenol system.

Using the resistances in series approach (Eq. (2) with $E = 1$), the stripping solution liquid film mass transfer coefficient (k_s) was calculated on the basis of the k_g and K_{ov}^0 values previously estimated, as $2.42 \times 10^{-6} \, \text{m s}^{-1}$ and also used as a model input.

The theoretical equilibrium constant for TEA, calculated from Eq. (11) as $5 \times 10^{10} \, \text{M}^{-1}$, is six orders of magnitude higher than that for phenol. Such a high K value implies that, at the operating pH (0.5–4.5), the expected concentration of neutral TEA in the stripping solution ($A_{s,b}$) is lower than $2 \times 10^{-6} \, \text{M}$. Using a stripping solution with a total TEA concentration of $2.36 \, \text{M}$ at pH 4.5, an equilibrium experiment (II.iii) was performed. The feed TEA concentration decreased over time to values below the detection limit of the analytical technique used ($10^{-5} \, \text{M}$), and thus it was impossible to estimate an experimental equilibrium constant. This experiment confirmed that the neutral TEA concentration in the stripping solution is negligible at pH < 4.5.

Using the above input parameters the enhancement factor was calculated according to the Hatta (Eq. (3)) and the Olander (Eq. (4)) models. The two models predict exactly the same mass transfer enhancement for the experimental conditions considered, as shown in Table 3. This observation is expected and consistent with the high TEA

Table 2
Summary of the experimental conditions and results for the TEA case study: average values of experimental overall mass transfer coefficients, stripping solution pH, inlet and feed solution concentrations

Time (day)	pH_s	Inlet: $A_{in}(M) \times 10^3$	Feed: $A_{f,b}(M) \times 10^3$	$K_{ov}(m\,s^{-1}) \times 10^6$
0–3	4.5	358.7 ± 7.7	214.9 ± 2.8	0.98 ± 0.07
4–7	1	336.7 ± 3.2	167.5 ± 2.2	1.48 ± 0.04
8–10	2	327.4 ± 3.7	169.7 ± 2.7	1.36 ± 0.04
11–13	3	339.0 ± 11.5	192.5 ± 7.4	1.11 ± 0.04
14–17	3	174.3 ± 5.9	99.8 ± 10.5	1.13 ± 0.04
18–22	3	8.8 ± 0.2	4.4 ± 0.3	1.47 ± 0.05
23–28	3	37.2 ± 1.3	19.9 ± 2.6	1.21 ± 0.05
29–36	3	78.3 ± 1.6	42.7 ± 2.1	1.22 ± 0.06
37–41	2	82.9 ± 0.8	41.4 ± 0.5	1.52 ± 0.05
42–45	1	81.2 ± 0.3	39.7 ± 1.1	1.50 ± 0.04
46–49	0.5	81.1 ± 1.1	39.1 ± 2.1	1.52 ± 0.04

Table 3
Ratios of TEA overall mass transfer coefficients measured experimentally and predicted by the Hatta and Olander models as a function of the stripping solution pH and feed concentrations

$A_{f,b}(M) \times 10^3$	pH_s				
	0.5	1.0	2.0	3.0	4.5
Experimental K_{ov}/K_{ov}^0					
168–218		1.59	1.46	1.19	1.05
99				1.21	
40	1.63	1.61	1.63	1.30	
20				1.31	
5				1.58	
Model predictions K_{ov}/K_{ov}^0 Hatta and Olander give the same prediction					
168–218		1.63	1.63	1.08	1.00
99	1.63	1.63	1.63	1.13	1.00
40	1.63	1.63	1.63	1.34	1.01
20	1.63	1.63	1.63	1.63	1.02
5	1.63	1.63	1.63	1.63	1.09

equilibrium constant and negligible neutral TEA concentration in the stripping solution at the experimental stripping solution pH values.

4.2.2. Mass-transfer measurements with chemical reaction

Experiment (II.iv), for K_{ov} measurements, was performed to estimate the overall mass transfer coefficient for TEA extraction at different fixed feed solution bulk concentrations and stripping solution pH. The experimental results obtained are shown in Fig. 5 and the average values with respective standard deviations are presented in Table 2. The K_{ov} calculations were performed assuming on $A_{s,b}$ of zero in Eq. (12), according to the equilibrium experiment (II.iii) results.

The overall mass transfer coefficient differences measured are significantly greater than the experimental error, showing that the chemical reaction mass transfer enhancement is significant in this system, and sensitive to the feed solution bulk concentration and the stripping solution pH. The experimental results are also presented in Table 3 as mass transfer coefficient ratios. On one hand, the mass transfer

enhancement is clearly pronounced with the stripping solution pH decrease. On the other hand, at a fixed stripping solution pH, the mass transfer coefficient increases as the feed bulk concentration ($A_{f,b}$) decreases. These experimental results are in a fair agreement with the trends of the models predictions also presented in Table 3. However, smoother transition to a maximum enhancement is observed in the experimental results at stripping solution pH 3. Generally the Hatta and the Olander model can be applied equally for mass transfer predictions for TEA and similar compounds.

The efficiency of TEA extraction from the feed solution was evaluated in two molar balances: (a) TEA in the stripping solution overflow, which evaluates the performance of TEA extraction at steady state and verifies for TEA losses or accumulations from and in the system; and (b) moles HCl added into the stripping solution, which confirms equimolarity of the acid–base reaction and the absence of side reactions in the stripping solution. Both cumulative molar balances closed within 5.9%.
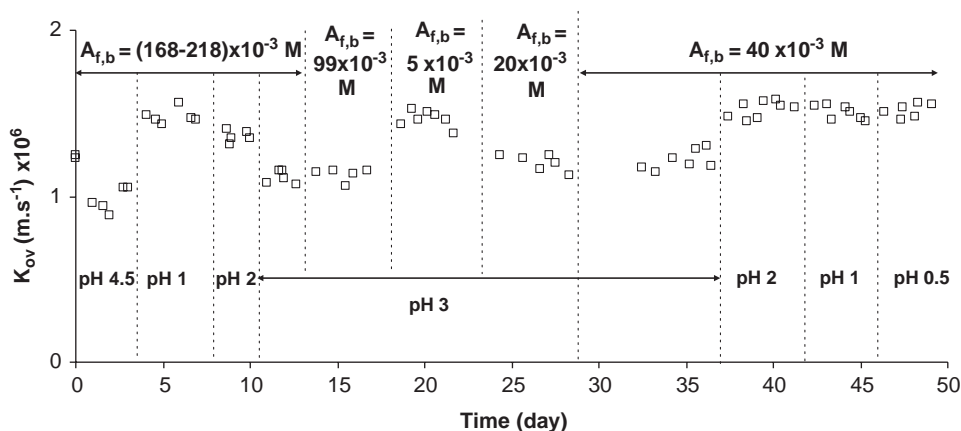
Fig. 5. Experimentally estimated overall mass transfer coefficients for TEA extraction over time at different feed solution TEA concentrations and stripping solution pH values.

4.3. 4-chlorophenol extraction

The aim of the experiments in this section was to measure mass transfer enhancement under conditions where there is a significant difference between the Hatta and the Olander model predictions. Experiments with 4CP were performed using an alkaline stripping solution maintained at a steady state organic concentration of 3.81 M via pH control through addition of a 6.15 M NaOH solution. This stripping solution has higher viscosity compared with the phenol and TEA experiments (Table 1), which results in a higher stripping solution liquid film resistance. Under these conditions, and since the membrane permeability for 4CP is about three times higher than that for phenol, is expected that the mass transfer is not controlled by the membrane resistance alone, and the effect of chemical reaction enhancement in the stripping solution should be measurable.

4.3.1. Model input parameters and model predictions

The overall mass transfer coefficient in the absence of chemical reaction (K_{ov}^0) was measured in a batch experiment (II.i), in which the stripping solution (see Fig. 3) was replaced with a solution of 2.58 wt% CMC, adjusted to pH 3. K_{ov}^0 was estimated using Eqs. (13) and (14) as $(3.1 \pm 0.1) \times 10^{-7}\,\mathrm{m\,s^{-1}}$, an average value of two measurements.

Similarly to TEA (experiment II.ii), k_g was taken as the maximum measured value of overall mass transfer coefficient, $4.1 \times 10^{-7}\,\mathrm{m\,s^{-1}}$, when the later does not increase further as $B_{s,b}$ increases (Table 4). Thus the maximum possible mass transfer enhancement for the 4CP system was estimated as $k_g/K_{ov}^0 = 1.3$.

The stripping solution liquid film mass transfer coefficient (k_s) was calculated as $1.24 \times 10^{-6}\,\mathrm{m\,s^{-1}}$, from Eq. (2) (with $E = 1$) using the k_g and K_{ov}^0 values estimated.

The 4CP equilibrium constant (K) value, as calculated from Eq. (11) (for $pK_a = 9.18$, (Lide, 1995)), is $7 \times 10^4\,\mathrm{M^{-1}}$. This value is close to that of phenol, implying that for a carefully chosen range of stripping solution pH, a significant fraction of the 4CP in the stripping solution is in neutral form. The theoretical neutral 4CP concentrations $A_{s,b}^{th}$, calculated from Eq. (10) for stripping solution with total 4CP content of 3.81 M and for the three stripping solution pHs experimentally employed: 11.7, 12.2 and 13.4 are listed in Table 4. However, due to thermodynamic considerations and possible deviations from ideal behaviour, as for the previous compounds the corresponding equilibrium experimental values were also determined (equilibrium experiment II.iii) and are listed in Table 4. The measured values of $A_{s,b}^{exp}$, are in poor agreement with the theoretically calculated ones ($A_{s,b}^{th}$).

The use of an accurate value for $A_{s,b}$ is important since this value has to be taken into account in the driving force for the K_{ov} value estimation in the experiment with chemical reaction (Eq. (12)). Moreover, as already mentioned the equilibrium constant (K) is also a key parameter in the Olander model. Therefore a new value for the equilibrium constant was estimated from Eq. (15) (re arranged Eq. (10)) based on the experimental $A_{s,b}^{exp}$

$$\frac{C_{s,b}^T}{A_{s,b}^{exp}} - 1 = K B_{s,b}. \tag{15}$$

Linear representation of Eq. (15) is shown in Fig. 6, in which the value for the experimental equilibrium constant is estimated as $2 \times 10^4\,\mathrm{M^{-1}}$. This is quite different from the one calculated from pK_a in literature, $7 \times 10^4\,\mathrm{M^{-1}}$. Similarly to the estimated equilibrium constant for phenol, the differences between theoretical and experimental values might be attributed to the high organic concentration and ionic strengths of the stripping solution, the operating temperature of 30 °C used and perhaps inaccuracy of pH measurements. The experimentally estimated equilibrium constant value (K^{exp}) was used as a model input.

k_g, k_s, K^{exp} and the diffusion coefficients (Table 1) were used for the Hatta and the Olander model mass transfer enhancement calculations shown in Table 4. As was

Table 4
Summary of the experimental and theoretical results for the 4CP case study

pH_s	Neutral 4-chlorophenol (M) $\times 10^3$				$K_{ov} \times 10^7$	K_{ov}/K_{ov}^0		
	Inlet: A_{in}	Feed: $A_{f,b}$	$A_{s,b}^{exp}$	$A_{s,b}^{th}$	(m s^{-1})	Exp.	Hatta	Olander
11.7	172.0 ± 3.2	95.0 ± 1.8	29.7	10.8	3.3 ± 0.1	1.1	1.3	1.1
	75.3 ± 1.7	50.0 ± 1.0			3.3 ± 0.2	1.1	1.3	1.1
12.2	69.6 ± 1.8	33.6 ± 0.9	9.4	3.4	4.1 ± 0.1	1.3	1.3	1.3
	174.0 ± 3.4	75.7 ± 1.7			4.1 ± 0.2	1.3	1.3	1.3
13.4	169.0 ± 7.9	68.9 ± 2.9	0.7	0.2	4.1 ± 0.2	1.3	1.3	1.3
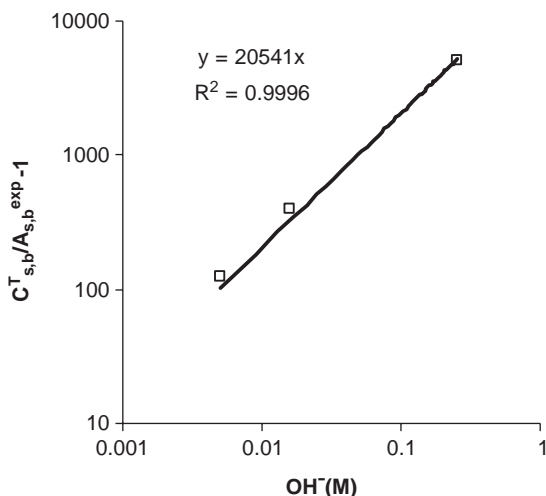
Fig. 6. Linear regression for estimation of experimental equilibrium constant for 4CP.

Fig. 7. Experimentally estimated overall mass transfer coefficients for 4CP extraction over time at different stripping solution pH values.

expected for the 4CP system, there is a range of conditions, where the two models predict different mass transfer enhancement.

4.3.2. Mass-transfer measurements with chemical reaction

Experiment (II.iv) was performed to estimate overall mass transfer coefficient (K_{ov}) for 4CP extraction at different feed solution bulk concentrations ($A_{f,b}$) and stripping solution pH values. The experimental results are shown in Fig. 7, and the average values for K_{ov}, with respective standard deviations, are presented in Table 4. Both terms in the organic flux equation (Eq. (1)), i.e., the driving force and the mass transfer coefficient, will be affected by the chemical reaction. The influence on the driving force was accounted for, by using the experimentally measured $A_{s,b}$ values at different stripping solution pH values (Table 4). Therefore, comparison of estimated mass transfer coefficient values at different operating conditions reflect the effect of chemical reaction on the mass transfer resistance only.

The experimentally obtained K_{ov} values at three different stripping solution pH values, together with the corresponding Hatta and Olander model mass transfer enhancement predictions, expressed as mass transfer coefficients ratios, are presented in Table 4.
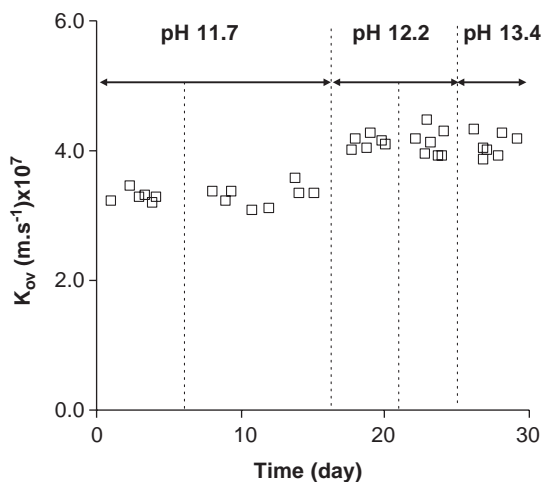
The experimental results show that increasing the stripping solution pH from 11.7 to 12.2 leads to a significant enhancement in mass transfer coefficient (3.3×10^{-7} vs. 4.1×10^{-7} m s^{-1}). This is consistent with the Olander model calculations, but deviates significantly from the Hatta model, which yet predicts maximum enhancement at pH 11.7. Further increase in pH from pH 12.2 to 13.4, does not affect the K_{ov} value, and thus it is evident that the maximum enhancement has been reached. Under maximum enhancement conditions both models describe well experimental results.

For the experimental conditions employed, and fixed stripping solution pH, the mass transfer coefficients were equal for the different feed bulk concentrations ($A_{f,b}$) tested. Ferreira et al. (2004) demonstrated that both models predict that the overall mass transfer coefficient increases as $A_{f,b}$ decreases. However, because the interval of experimental feed solution concentrations is too narrow in the present study, the above effect is observed neither experimentally nor theoretically. The choice of these $A_{f,b}$ values is restricted to between the aqueous solubility limit (~ 0.21 M) of 4CP and, a feed solution bulk concentration ($A_{f,b}$) above $A_{s,b}$, in order to maintain the driving force for 4CP extraction.

The experimental results confirmed that for compounds with moderate equilibrium constant such as 4CP, there are ranges of operating conditions where the Hatta model still can give a fair prediction, in particular when $B_{s,b}$ is high enough that the neutral organic concentration in the stripping solution still can be neglected. However, for such compounds, in most of the cases, the Olander and Hatta model predictions for the mass transfer coefficient enhancement are close enough (Table 4), but $A_{s,b}$ is not necessarily negligible for the mass transfer bulk driving force. Such is the case for the 4CP extraction with $A_{f,b}$ of 33.6×10^{-3} M and stripping solution at pH 12.2. In this example a value of 9.4×10^{-3} M for the $A_{s,b}$ concentration, implies a difference in the driving force of 28%. The Hatta and Olander model predictions can deviate even further, as for example in a more sensitive case, illustrated with 4CP, in which the Hatta model overestimates both the mass transfer enhancement and the driving force, and predicts a maximum mass transfer coefficient value at pH 11.7, whereas, the Olander model (confirmed by the experimental results) predicts an intermediate enhancement value at this pH. In the latest case the Hatta model generates error as high as 42% in the flux calculations for the feed solution 4CP concentration of 95.0×10^{-3} M. Similarly to the TEA system, molar balances for 4CP extracted from the feed solution closed within 4.0 %.

5. Conclusions

This work shows experimentally that the chemical reaction mass transfer enhancement plays an important role in the MARS extraction stage. Maximum overall mass transfer coefficients enhancements of ~1.6 and ~1.3 were measured, corresponding to potential savings in the membrane area of ~38% and ~23%, for triethylamine and 4-chlorophenol extraction, respectively. For cases such as phenol, where the membrane mass transfer resistance dominates the system, there is no significant mass transfer enhancement.

As the contribution of stripping solution liquid film resistance to the overall mass transfer resistance increases, the mass transfer enhancement due to chemical reaction becomes increasingly important, and therefore these effects will be significant in larger scale MARS applications.

The experimental results showed that for organic acids and bases with high equilibrium constant such as TEA, the Hatta and the Olander models can be applied equally, and the chemical reaction can be assumed irreversible. It was also experimentally confirmed that the mass transfer enhancement increases with an increase of the concentration of free ionic reagent in the stripping solution ($B_{s,b}$) and with a decrease of the feed organic concentration ($A_{f,b}$). This behaviour follows the trends predicted by the models.

Conditions under which the Hatta and Olander models predict different mass transfer enhancements were identified. One such case was evaluated using 4CP at pH 11.7. For this case, the experimental results showed that the Hatta model overpredicts mass transfer enhancement. Hence, in spite the mathematical simplicity of the Hatta model, the authors recommend the use of the Olander model for mass transfer predictions and optimisation of MARS process. This is especially so in light of the analytical solution for the Olander model developed in the preceding paper, which will assist in such calculations.

Notation

A	transported solute, neutral, M
AB	reaction product, monovalent, M
B	second reactant, monovalent, M
C	concentration, M
CMC	carboxymethyl cellulose
D	diffusion coefficient, $m^2 s^{-1}$
E	mass transfer enhancement factor, dimensionless
F	flow rate, $L s^{-1}$
I_m	membrane area, m^2
J	flux, $mol s^{-1}$
k_f	feed solution liquid film mass transfer coefficient, $m s^{-1}$
k_g	grouped mass transfer coefficient, $m s^{-1}$
k_m	membrane mass transfer coefficient, $m s^{-1}$
k_s	stripping solution liquid film mass transfer coefficient, $m s^{-1}$
K	equilibrium constant, M^{-1}
K_a	organic acid dissociation constant, M
K_{ov}	overall mass transfer coefficient, $m s^{-1}$
K_{ov}^0	overall mass transfer coefficient in the absence of chemical reaction, $m s^{-1}$
K_w	water auto-ionisation constant, M^2
Mw	molecular weight, $g mol^{-1}$
P	permeability, $m^2 s^{-1}$
S	organic stripping solution
t	time, s
TEA	triethylamine
V	volume, L
4CP	4-chlorophenol

Greek letters

δ	thickness, m
μ	viscosity, cP
ρ	density, $kg L^{-1}$

Subscripts and superscripts

0	in the absence of chemical reaction
add	ionic reagent added
A	referred to the transported solute
AB	referred to the reaction product
b	in the bulk of the solution
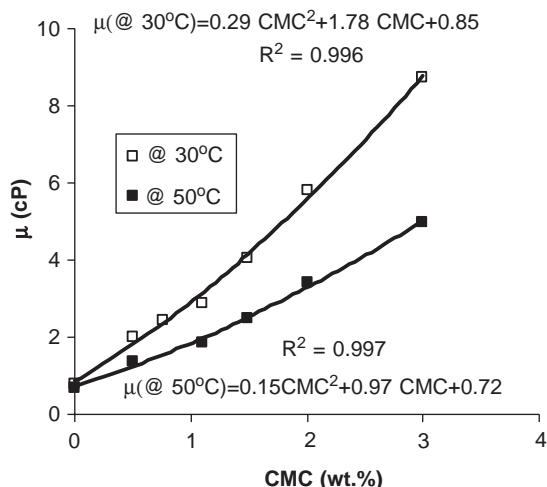
Fig. 8. Viscosity calibration for different CMC concentrations at 30 and 50 °C.

B	referred to the second reactant
exp	experimental
f	feed solution
i	at membrane/stripping solution interface
in	inlet solution
m	membrane
ov	overall
s_{out}	stripping solution overflow
s	stripping solution, reactant phase
th	theoretical
T	total organic, the sum of both forms, neutral (A) plus ionic (AB)

Acknowledgements

Appendix

Viscosity calibration for different CMC concentration is shown in Fig. 8.

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