

## Carboxylic acids separation using hollow fiber supported liquid membrane

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The experimental and modeling studies for extraction of different carboxylic acids using hollow fiber supported liquid membrane operated in a recycle mode has been described here. Characterization of membrane has been carried out to find the pore size. Tri-*n*-butyl phosphate (TBP), tri-*n*-octylamine (TOA) and tri-*n*-octylphosphine oxide (TOPO) are used as extractants for extraction studies. A generalized methodology for the extraction of carboxylic acids has been proposed. The extraction equilibrium studies for carboxylic acids are carried out to find the distribution coefficient ( $k_d$ ) and the equilibrium constant ( $K_{ex}$ ). A mathematical model has been developed by considering the mass transfer as well as the complexation and de-complexation reactions. The equilibrium results show that the extractants plays an important role in extraction of carboxylic acids, and thus influence the extraction of carboxylic acids. Almost 99% extraction of carboxylic acids has been achieved using 1% TOPO as an extractant. Effect on transport of carboxylic acids under various conditions, including acid concentrations, extractant concentrations, feed/strip flow rate, feed volume, scale up etc. has been investigated. Scale-up experiment show that flux obtained at both scales is the same and hence the rate of extraction is significantly faster in a module with high surface area.

**Keywords:** Equilibrium, Mass transfer, Mathematical modeling, Membranes

Recovery of low molecular weight carboxylic acids such as acetic acid (AA), phenylacetic acid (PAA), formic acid (FA) etc. from dilute aqueous stream has received increasing attention because of their application in various fields<sup>1-4</sup>. Carboxylic acids are the most important organic pollutants discharged from industrial sources. The main sources of the carboxylic acids include manufacture of cellulose acetate, chemical pulping of wood, and the waste from petrochemical industries<sup>5,6</sup>. Most of the carboxylic acids such as phenylacetic acid, citric acid etc. are produced from the fermentation processes and widely used in pharmaceutical industries<sup>7</sup>. Therefore, pharmaceutical waste is also an important source of carboxylic acids. Concentration of the carboxylic acids in the waste vary from 0.1% to 5% by weight; if discharged to water bodies it results in the increase of oxygen demand<sup>8</sup>. Hence, carboxylic acid extraction is of immense industrial importance. From a practical point of view, it is important not only to extract carboxylic acid but also to concentrate it.

Extraction of carboxylic acids has been studied by a number of researchers using conventional techniques such as, extractive distillation<sup>8</sup>, reactive distillation<sup>9</sup>, liquid-liquid extraction<sup>10</sup> (Table 1),

supported liquid membrane pervaporation (SLMPV)<sup>11</sup>. Distillation processes for carboxylic acids recovery are economical, only if the acid concentration in the aqueous stream is in the range of 30-80% by weight<sup>8</sup>. At low concentration of carboxylic acids, the relative volatility is close to unity. Thus, the separation by distillation is very energy intensive at low acid concentrations. In liquid-liquid extraction the solvent required for separation is very high. SLMPV is a pervaporation process for separating volatile organic compounds (VOCs) from their dilute aqueous solution. Qin et al.<sup>11</sup> employed this technique for the separation of acetic acid from its mixture. Supported liquid membranes (SLM) are a promising, alternative and energy efficient technique for acetic acid extraction over these conventional methods.

In the recent years, membrane separation processes have gained considerable attention due to their low solvent inventory, less extractant consumption, cost effectiveness and single unit separation. Supported liquid membranes (SLM) have been extensively studied as an important process for retrieving acids<sup>12-15</sup>, pharmaceutical components<sup>16,17</sup>, and radioactive metals<sup>18-21</sup> from effluent stream. SLM

Table 1 — Previous literature on equilibrium study of carboxylic acids

Extractant*	Carboxylic acid	$k_d$	Diluent	Reference
Chloroform	Acetic acid	0.0075	<i>n</i> -Heptane	Tamada <i>et al.</i> <sup>4</sup>
TOPO(18% w/w)	Acetic acid	1.165	Kerosene	Golob <i>et al.</i> <sup>10</sup>
TBP	Acetic acid	1	Hexane	Fahim <i>et al.</i> <sup>36</sup>
TOA		0.45		
TBP	Acetic acid, Lactic acid,	1.8	Hexane	Matsumoto <i>et al.</i> <sup>37</sup>
TOA	Glycolic acid, Propionic acid,	0.7		
	Acetic acid, Lactic acid,	0.3		
	Glycolic acid, Propionic acid	7		
		0.06		
		0.05		
		0.03		
		0.36		
TOA	Citric acid	23	Decanol	Wasewar <i>et al.</i> <sup>38</sup>
Aliquat 336	Acetic acid	0.996	Kerosene	Yang <i>et al.</i> <sup>39</sup>
TOA	Citric acid	1.99	1-Octanol	Prasanna Rani <i>et al.</i> <sup>40</sup>
TBP (15.2% w/w), DBP (13.5% w/w), TBPO (12.5% w/w), TPPO (6.4 % w/w)	Acetic acid (0.5M)	0.28 0.45 2.1 0.16	Chevron solvent 25 (approximately mixture of C <sub>9</sub> alkyl aromatics) <i>n</i> -Hexanol	Wardell <i>et al.</i> <sup>41</sup>
Tributylamine (3.84% w/w), Triisooctylamine (7.52% w/w)		0.34 5.3		

\*TBP=Tri-*n*-butylphosphate, TOA=Tri-*n*-octylamine, TOPO=Trioctylphosphine oxide, DBP=Dibutyl butylphosphonate, TBPO = Tributylphosphine oxide, TPPO=Triphenylphosphine oxide

studies have become very popular all over the world ever since their invention by Li and co-workers in the 1960s<sup>22</sup>. The important feature of this membrane is that it provides high surface area to volume ratio for maximum solute flux per unit volume<sup>23</sup>.

The organic extractants such as aliphatic amines (tripropylamine, tri-*n*-octylamine etc.) and phosphorous compounds (TBP, TOPO etc.) have been used mainly for the carboxylic acids extraction<sup>24</sup>. Hong *et al.*<sup>25</sup> discussed on selective separation of carboxylic acids using phosphorous and amine based extractants. Selective separation of succinic acid from succinic and acetic acid aqueous mixture with amine based extractants has been reported<sup>26</sup>. Some of the researcher found that the TOPO extractant diluted with hexane or kerosene solvent is the optimum extractant for carboxylic acids separation in membrane based extractive fermentation<sup>27,28</sup>.

The use of supported liquid membranes to carry out simultaneous extraction and stripping using one contactor has been reported in the past. However, these studies merely report experimental results on extraction of carboxylic acids with various extractants

and under various operating conditions. There are practically no studies that report comprehensive mathematical model and scale-up study. These were the objectives of the present work. The novelty of this work lies in the systematic methodology: (i) liquid – liquid extraction experiments are carried out to measure the distribution coefficient of carboxylic acids under various conditions, (ii) The distribution of carboxylic acid is written in terms of a complexation reaction and equilibrium constant is found out, (iii) characterization of membrane for measurement of pore size, (iv) Development of a common framework for mathematical modeling of hollow fiber supported liquid membranes (HFSLM) and (v) scale-up aspects.

## Experimental Section

### Materials

Carboxylic acids such as acetic acid (99.9% glacial), formic acid (98% AR) and phenylacetic acid (pure) were purchased from S.D.Fine Chemical Ltd. India. Organic solvents such as tri-*n*-butyl phosphate (TBP), tri-*n*-octylamine (TOA) and tri-*n*-octylphosphine oxide (TOPO) were obtained from S. D. Fine

Chemical Ltd. India. Sodium hydroxide (NaOH), kerosene and dodecane were also purchased from S.D.Fine Chemical Ltd. India. All the chemicals were used without further purification. Hollow fiber polypropylene (PP) membrane modules were procured from Membrana USA. Liqui-Cel X50 (2.5 x 8) and Liqui-Cel-X50 (4 x 13) type modules were used in the present work. The details of these modules are given in Table 2.

#### Characterization of membranes

The membrane characterization was carried out for the determination of average pore size and breakthrough pressures of hollow fiber PP membrane. Pore size is an important parameter as it governs the rate of diffusion through the membrane. Breakthrough pressure is an important operating consideration for use of supported liquid membranes. Pore size is determined in two ways: (i) measurement of flux at various pressures and (ii) measurement of breakthrough pressure.

#### Hollow fiber flux measurement

The experimental set up for the flux measurement through the hollow fiber PP membrane is schematically represented in Fig. 1. Lumen side (fiber) outlet of the module was kept closed during the experiments and the solvent (water or dodecane) was passed through the lumen side inlet of the module. Pressure was applied over the solvent inside feed tank, so that permeation occurred through the hollow fiber PP membrane. The permeated liquid was collected at regular interval of time. The experiments were performed at different gauge readings. The

water and dodecane fluxes were calculated from the permeate flow of water and dodecane through the hollow fiber membrane. Since the membrane is highly hydrophobic, dodecane completely wets the membrane and its flux allows the calculation of pore size by the use of Hagen-Poiseuille equation. On the other hand, water being non-wetting allows measurement of breakthrough pressure.

The relationship between flux ( $J$ ) of dodecane and the applied pressure difference ( $\Delta P$ ) is given by the Hagen-Poiseuille equation<sup>29</sup>.

$$\Delta P = \left( \frac{32 \mu}{d^2} \right) J \quad \dots(1)$$

where,

$J = Q/A_m$ , is the flux (kg/m<sup>2</sup>.s)

$Q$  is the permeate mass flow rate (kg/s)

$A_m$  is the membrane effective area (m<sup>2</sup>)

$\mu$  is the viscosity of fluid (kg/m.s)

$\Delta P$  is the pressure difference (N/m<sup>2</sup>)

The pore size of the membrane was calculated from the slope of plot between permeate mass flow rate ( $Q$ ) and pressure difference ( $\Delta P$ ).

As the water is non-wetting liquid for the PP membrane, the average pore size of the PP membrane was calculated from the breakthrough pressure. The relationship between breakthrough pressure ( $P$ ) and contact angle ( $\theta$ ) can be expressed by Young-Laplace equation<sup>30</sup>. This enables calculation of the pore size from the measured breakthrough pressure.

$$P = - \frac{4 \sigma \cos \theta}{d} \quad \dots(2)$$

Table 2 — Specifications of HFSLM modules for the carboxylic acids extraction experiments

Membrane type	PP X50 (2.5x8)	PP X50 (4x13)
Number of fibers (N)	10,000	48,000
Fiber internal radius ( $r_i$ ), $\mu\text{m}$	100-120	100-120
Fiber outer radius ( $r_o$ ), $\mu\text{m}$	150	150
Effective module outer diameter ( $d_o$ ), cm	4.67	-
Effective module inner diameter ( $d_i$ ), cm	2.2	-
Effective pore size ( $r_p$ ), $\mu\text{m}$	0.03	0.03
Porosity ( $\epsilon$ ), %	40	40
Tortuosity ( $\tau$ )	2.5	2.5
Effective fiber length (L), cm	15	27
Typical membrane surface area (A), m <sup>2</sup>	1.4	8.1

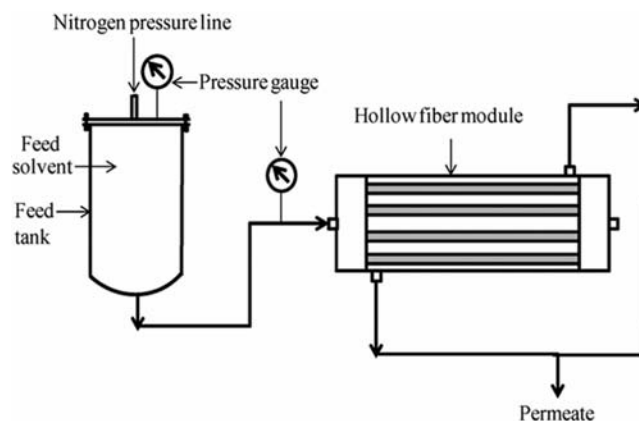


Fig. 1 — Schematic representation of the hollow fiber flux measurement set up.

### Equilibrium study

Equilibration experiments of different carboxylic acids were carried out to find the extraction equilibrium constants ( $K_{ex}$ ) and distribution coefficients ( $k_d$ ). Acetic acid, formic acid and phenylacetic acid were used in the present study for equilibrium experiments. Aqueous phases were prepared from the different carboxylic acids in deionized water. In practical situation of acid recovery from aqueous feed phase, the acid concentration is not expected to be high. Hence, lower concentration range (0.05-0.5M) of carboxylic acids was selected for the experiments. The physical properties of all these carboxylic acids are given in Table 3. Organic phases were prepared from the extractants like TBP, TOA and TOPO. Dodecane was used as solvent to dilute TBP and TOA as an extractant. Kerosene was used as solvent to dilute TOPO as an extractant.

Equal volumes (1.5 mL) of aqueous phases containing different carboxylic acid concentrations (0.05-0.5M) were mixed with the organic phases containing different extractant concentrations (0-50% TBP or TOA or TOPO (w/w)). After shaking the mixture vigorously for 1 hour, both the phases were allowed to settle and then separated by centrifuging at 1000 rpm. This speed is relevant to the force 100 g. Aqueous and organic phases containing acid were analyzed by using acid-base titration with 0.014 M NaOH solution. Phenolphthalein was used as an indicator. All the experiments were carried out at 298K.

### Transport of carboxylic acids through hollow fiber supported liquid membrane (HFSLM)

The hollow fiber experiments were carried out to find the transport behaviour of carboxylic acids with respect to different process parameters through HFSLM. The experimental set-up consisted of one

HFSLM module (X50 (2.5 × 8)), two reservoirs and two peristaltic pumps (one each for feed and strip solution). The set-up diagram is identical to our previous work<sup>31</sup>.

The liquid membrane phases were prepared by pumping organic extractants solution through the lumen side of the module in recirculation mode for 30 mins. Percolation of organic solution from the lumen to the shell side ensured proper soaking of all membrane pores. Aqueous feed and strip phases were prepared using different concentration of carboxylic acids and sodium hydroxide (pellet) into deionized water respectively. The experiments were carried out by varying the feed phase (0.05-0.5M acid) and the membrane phase (1-50%, EXTs) concentrations. 1M NaOH solution was used as strip phase for all the experiments.

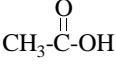
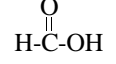
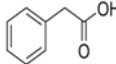
During the experimental runs, feed solution was passed through the lumen side whereas strip solution was passed through the shell side in a countercurrent flow. The exit solutions from the module were recycled back to the respective reservoirs. Approximately 2 mL of sample was taken from both the feed and the strip phase reservoirs at regular time intervals. The feed phase samples containing carboxylic acid were analyzed using dilute solution of NaOH (acid-base titration) with phenolphthalein as an indicator. NaOH solution was standardized using potassium hydrogen phthalate (KHP) before using it for the titrations. The transport behaviour of carboxylic acids was studied with respect to different process parameters such as, (a) Feed phase concentration, (b) Organic phase concentration (c) Different carboxylic acids, (d) Different organic extractants, (e) Feed/strip flow rate and (f) feed volumes.

The membrane fouling can be eliminated by removing the solid course particle, bacteria and dirt material from the feed solution using pre-filtration technique before performing the actual experiments. After finishing one set of extraction experiments; the washing treatment using water was done from both the lumen and shell sides of the module. This helps to prevent fouling inside membrane module.

### Scale up experiment

Acetic acid transport behavior was also studied by using a large scale HFSLM module. The detailed specifications of the large scale module (X50 (4 × 13)) are summarized in Table 2. Scale up experiment was performed in the same manner as

Table 3 — Physical properties of Carboxylic acids

Carboxylic acid	Structural formula	pK <sub>a</sub>	M.W (gm/mol)	Solubility in water at 25 °C
Acetic acid		4.76	60.05	miscible
Formic acid		4.31	46.03	miscible
Phenylacetic acid		4.77	136.15	15 gm/lit

described for X50 (2.5 × 8) contactor type. Feed and strip phase concentrations were taken as 0.3M acetic acid and 1M NaOH respectively. Membrane phase solution was taken as 50% TBP as an extractant diluted with n-dodecane. During the experimental run the volumes of feed and strip reservoirs were 1000 ml and 2000ml respectively. The flow of feed and strip solutions through lumen and shell side was maintained constant at 500ml per minute in counter-current mode. The concentration data obtained from this experiment was used for the calculation of percent transport of acetic acid.

#### Mathematical model

The assumptions made to describe the transport process of a solutes (acid molecules) through HFSLM have been mentioned in elsewhere<sup>31</sup>.

In recycle mode operation, both the feed and strip phases were continuously recirculated in countercurrent mode through the HFSLM module using peristaltic pumps. Assuming reservoir tanks to be well mixed, mass balance across the feed / strip reservoirs may be expressed as,

$$V_f \frac{dC_{f0}}{dt} = Q_f (C_{fz} - C_{f0}) \quad \dots(3)$$

$$V_s \frac{dC_{s0}}{dt} = Q_s (C_{sz} - C_{s0}) \quad \dots(4)$$

To solve these equations we need to relate the feed side inlet concentrations ( $C_{f0}$ ) and exit concentrations ( $C_{fz}$ ) by applying steady state mass balance along the module length which is explained in the sections below.

#### Module exit concentration

The acid present in the feed phase is extracted into the organic phase by physical extraction, diffusion through the fiber and then stripped into the strip phase by de-complexation reaction.

Steady state material balance of moles of acid<sup>32</sup> across the differential element is expressed as,

$$-Q_f \cdot dC_f = R_T \cdot N \cdot r_{if} \cdot dz \quad \dots(5)$$

The above equation can be modified in terms of lumen (fiber) velocity ( $u_f$ ) as,

$$\frac{dC_f}{dz} = -R_T \cdot \frac{2}{r_{if} \cdot u_f} \quad \dots(6)$$

Steady state concentration profile across all the resistances is reported in literature<sup>31</sup>. The carboxylic acid transfer flux ( $R_T$ ) from feed phase to membrane phase follows the steps described below.

(i). Rate of diffusion ( $R_T$ ) of acid from the bulk of feed phase to the feed-membrane interface is,

$$R_T = k_f (C_f - C_{if}) \quad \dots(7)$$

(i). Rate of diffusion ( $R_T$ ) of acid inside the membrane pore will be equal to the rate of diffusion ( $R_{TCM}$ ) of acid-extractant complex from the feed-membrane interface to the strip-membrane interface is,

$$R_T = R_{TCM} = \frac{D_m}{d_o} (C_{imf} - C_{ims}) \quad \dots(8)$$

The strip side resistance in the hollow fiber module has been neglected due to the formation of sodium acetate.

Overall mass transfer flux ( $R_T$ ) from the feed phase to the strip phase has been calculated by solving the Eq.(7) and (8).

$$R_T = \frac{C_f}{\frac{1}{k_f} + \frac{d_o}{D_m} \left( \frac{1}{k} \right)} = K \cdot C_f \quad \dots(9)$$

'K' is defined as the overall mass transfer coefficient of the transport process.

$$\frac{1}{K} = \frac{1}{k_f} + \frac{d_o}{D_m} \left( \frac{1}{k} \right) \quad \dots(10)$$

The module exit concentration ( $C_{fz}$ ) of the feed phase acid can be solved by substituting Eq. (9) into Eq. (6),

$$dC_f = -K \cdot C_f \cdot \frac{2}{r_{if} \cdot u_f} dz \quad \dots(11)$$

Boundary conditions:

B.C. 1: At  $z = 0$ ,  $C_f = C_{f0}$ ,

B.C. 2: At  $z = L$ ,  $C_f = C_{fz}$ ,

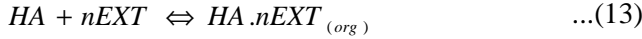
Eq. (11) is integrated with the above boundary conditions (B.C. 1 and 2) considering  $K$  to be constant with respect to 'z' at any given time. The resulting equation for feed phase module outlet concentration is,

$$C_{fz} = C_{f0} \cdot \exp\left(\frac{-2 \cdot K \cdot L}{r_{if} \cdot u_f}\right) \quad \dots(12)$$

To evaluate  $K$ , the model parameters ( $K_{ex}$ ,  $k_f$  and  $D_m$ ) have been calculated as explained in section below.

#### Estimation of model parameters ( $K_{ex}$ , $k_f$ and $D_m$ )

Acid complex formation reaction can be written as,



where,  $HA$  stands for carboxylic acid and  $[HA \cdot nEXT]_{(org)}$  is the acid-extractant complex.

The extraction equilibrium constant ( $K_{ex}$ ) is expressed as,

$$K_{ex} = \frac{[HA \cdot nEXT]_{org}}{[HA]_{aq} \cdot [EXT]_{free,org,f}^n} \quad \dots(14)$$

The reaction equilibrium on the feed-membrane interface is,

$$K_{ex} = \frac{C_{imf}}{C_{if} \cdot [EXT]_{free,org,f}^n} \quad \dots(15)$$

Mass balance of the extractant ( $EXT$ ) in the membrane phase may be expressed as,

$$[EXT]_{initial,org} = [EXT]_{free,org} + n[Acid - Complex]_{org} \quad \dots(16)$$

Distribution coefficient ( $k$ ) has been calculated from Eq. (15),

$$k = K_{ex} \cdot [EXT]_{free,org}^n = \frac{C_{imf}}{C_{if}} \quad \dots(17)$$

The flow through the lumen is usually very small, resulting in low values of Reynolds number. Hence, following correlation<sup>33</sup> was used to evaluate  $k_f$  for laminar flow condition.

$$\left(\frac{d_i k_f}{D}\right) = 1.128 \left(\frac{d_i^2 u_f}{LD}\right)^{1/2} \quad \dots(18)$$

Since the feed phase was dilute solution of the carboxylic acid, Wilke-Chang Eq. (19) was used to determine diffusivity ( $D$ ) of the acid (A) through the solvent (B)<sup>34</sup>.

$$D = \frac{117.3 \times 10^{-18} (M_B)^{0.5} T}{v_A^{0.6}} \quad \dots(19)$$

Membrane diffusivity ( $D_m$ ) signifies diffusion coefficient of the acid-complex diffusing through the supported liquid membrane. In the present work,  $D_m$  was estimated by fitting the developed model with the base case of single experiment and the same has been used for the validation of model.

## Results and Discussion

#### Calculation of pore size for hollow fiber membrane

The relationship between permeate mass flow rate ( $Q$ ) and transmembrane pressure difference ( $\Delta P$ ) across hollow fiber PP membrane is given by Eq. (1). It can be seen from this study that for a given applied pressure differential, the flux of dodecane through the hollow fiber membrane is substantially higher than the water flux. The value of average pore diameter for hollow fiber PP membrane was calculated from the slope of Eq. (1). The calculated value of slope using dodecane as solvent was  $1.94 \times 10^{-4}$  (kg m<sup>2</sup>/N-s). The pore diameter calculated from dodecane flux thus comes out to be ~0.01  $\mu$ m.

The measured value of contact angle ( ) between deionized water and PP membrane was 130°. It confirmed the hydrophobic nature of the PP membrane. The relationship between breakthrough pressure and pore diameter is given by Eq. (2). The measured value of breakthrough pressure of water through the hollow fiber PP membrane was 32,000 N/m<sup>2</sup>. Using Eq. (2), the calculated value of pore diameter with the breakthrough pressure was found to be 2.33  $\mu$ m. This indicates that there is a wide variation between the pore size calculated through the measurements of dodecane mass flow rate and the water breakthrough pressure. The measurement of pore size obtained through dodecane flux is a combined effect of all the pores that contribute to the flow of dodecane. Whereas, the breakthrough of water for hollow fiber PP membrane is likely to happen first for the largest pores. Hence the measured value of pore size through breakthrough pressure is an indication of the largest pore size in the membrane. For application of SLM technique, both the values are important. The measured flux is an indication of the rate of diffusion through the hollow fiber PP membrane, whereas the breakthrough pressure places a constraint on the maximum operable transmembrane pressure differential.

### Equilibrium study

Distribution of carboxylic acids was studied by performing the equilibrium experiments with TBP, TOA and TOPO as an extractants. Figures 2a and b shows the relationship between distribution coefficients ( $k_d$ ) and equilibrium acid concentrations ( $HA$ ) for Acetic acid-TBP and Acetic acid-TOA systems respectively. It can be seen from the figure that the distribution coefficients ( $k_d$ ) of acetic acid increased with an increase in extractant concentrations. It showed higher values of  $k_d$  for TBP as an extractant (0.1-0.82) compared to TOA as an extractant (0.05-0.26). At lower acid concentrations, large numbers of extractant molecules were available for complexation with acid molecules. Hence the value of  $k_d$  was higher with lower acid concentration compared to that with higher acid concentration.

Extraction equilibrium constants ( $K_{ex}$ ) of acetic acid were calculated from the slope of complex

organic concentration versus product of aqueous acid and free extractant concentration at equilibrium using Eq. (14). Figures 2c and d shows the relationship between extraction equilibrium constant ( $K_{ex}$ ) and the product of equilibrium acid concentrations ( $HA$ ) and free extractant concentration for TBP and TOA as an extractants respectively. Plot exhibit a linear relationship. The  $K_{ex}$  value obtained for the acetic acid was higher for TBP extractant ( $0.463 \text{ kmol}^{-1} \text{ m}^3$ ) compared to TOA extractant ( $0.171 \text{ kmol}^{-1} \text{ m}^3$ ). The values of  $K_{ex}$  obtained for the different extractants were used in model predictions. Similar methodology was adopted for the remaining sets of equilibrium experiments for various carboxylic acids. The comparative study of all these carboxylic acids is given in Table 4.

It can be seen from the Table 4 that,  $K_{ex}$  values obtained for all the acids along with TOPO as an extractant were observed higher compared to TBP and

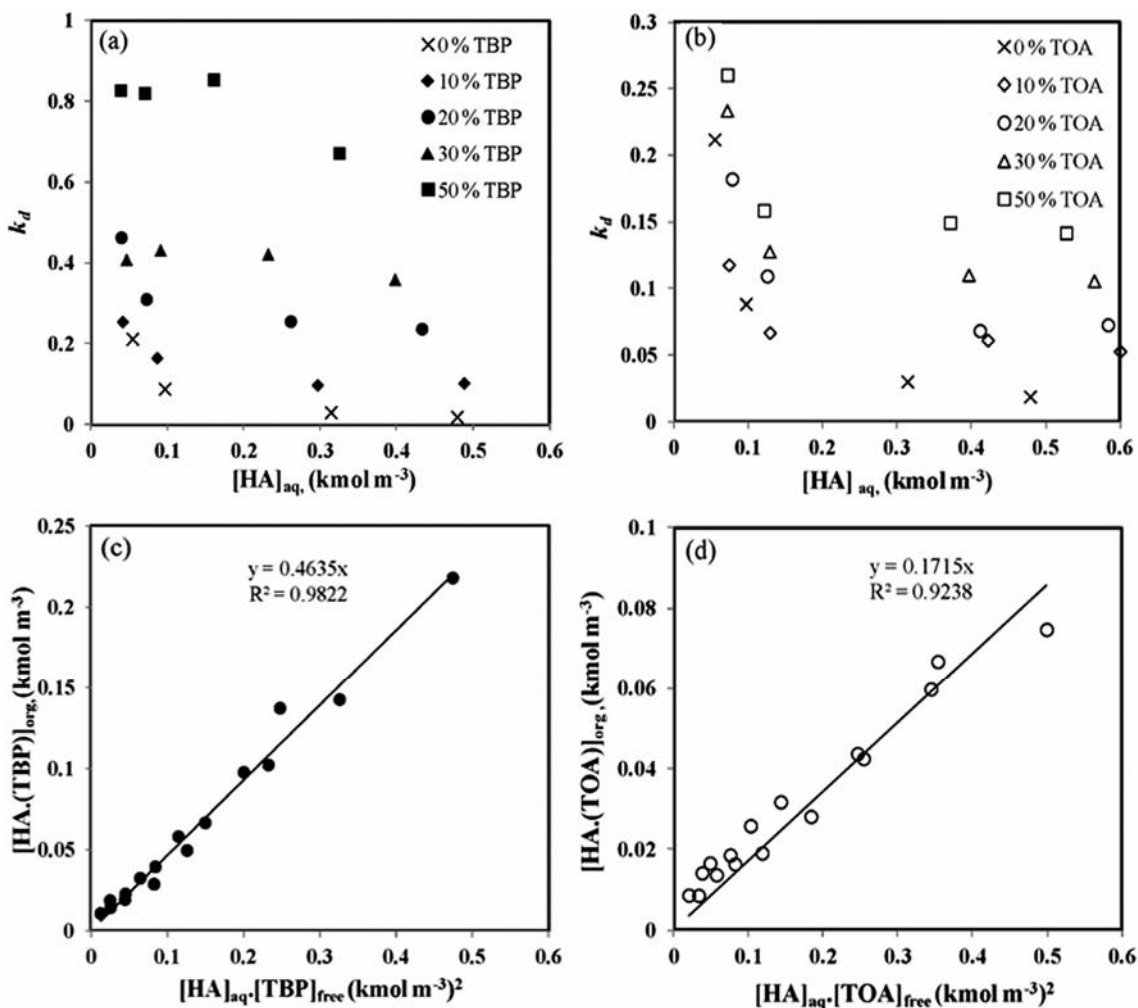


Fig. 2 — Distribution coefficient ( $k_d$ ) and extraction equilibrium constant ( $K_{ex}$ ) for acetic acid- EXTs (TBP or TOA) system

Table 4 — Comparative study of carboxylic acids



Carboxylic acid	Extractant	Stoichiometry (m : n)	$K_{ex}$ (m <sup>3</sup> /kmol)	Membrane diffusivity ( $D_m$ ), m <sup>2</sup> /sec	*Initial flux (kmol/m <sup>2</sup> hr)
HCOOH	TBP	1 : 1	0.652	$1.0 \times 10^{-10}$	$1.002 \times 10^{-5}$
	TOA	1 : 1	0.297	$3.0 \times 10^{-10}$	$0.825 \times 10^{-5}$
	TOPO	1 : 1	5.686	$1.5 \times 10^{-10}$	$8.55 \times 10^{-5}$
CH <sub>3</sub> COOH	TBP	1 : 1	0.463	$0.6 \times 10^{-10}$	$1.022 \times 10^{-5}$
	TOA	1 : 1	0.171	$5.0 \times 10^{-10}$	$0.784 \times 10^{-5}$
	TOPO	1 : 1	4.395	$1.2 \times 10^{-10}$	$4.234 \times 10^{-5}$
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOH	TBP	1 : 1	21.94	$0.9 \times 10^{-10}$	$16.81 \times 10^{-5}$
	TOA	1 : 1	12.93	$2.2 \times 10^{-10}$	$13.18 \times 10^{-5}$
	TOPO	1 : 1	74.06	$6.0 \times 10^{-10}$	$39.42 \times 10^{-5}$

TBP=Tri-n-butylphosphate, TOA=Tri-n-octylamine, TOPO=Tri-n-octyl phosphine oxide, HA=Carboxylic acid, EXT=Extractant, m=Moles of acid, n=Moles of extractant

\*Initial flux values of all these acids have been calculated at 0.05M HA and 1% (w/w) EXT concentration

**Note:** Dodecane was used as diluent for all the experiments except for TOPO extractant kerosene was used as diluent.

TOA. The decreasing order of  $K_{ex}$  values obtained for different extractants is TOPO>TBP>TOA. The decreasing order of the basic strength for these organic extractants is reported in literature<sup>35</sup>. TOPO and TBP extractant forms the complexes with carboxylic acids through donating the electrons but TOA mostly forms the complex using sharing of ionic strength<sup>36</sup>. Hence the  $K_{ex}$  values obtained for TOPO extractant was higher compared to TBP and TOA.

The physical properties of the carboxylic acids are shown in Table 3. The decreasing order of strength of carboxylic acid based on  $pK_a$  values is FA > PAA > AA. But, the decreasing order of  $K_{ex}$  was observed as PAA > FA > AA. The solubility of PAA in water is 15g/L (Table 3). Lower solubility of PAA in water led to higher extraction. Hence,  $K_{ex}$  values obtained for PAA were higher compared to FA and AA.

#### Model predictions for the base case in HFSLM

The experimental data generated with initial concentration of 0.3M acetic acid and 10% TBP as an extractant was selected as base case (Fig. 3a). The values of feed side diffusivity ( $D$ ) and film mass transfer coefficient ( $k_f$ ) of acetic acid molecules through HFSLM were calculated using previously discussed correlations (Eqs. (18) and (19)). The values of  $D$  and  $k_f$  were  $1.2417 \times 10^{-9}$  m<sup>2</sup>/s and  $1.117 \times 10^{-5}$  m/s respectively. The value of membrane diffusivity ( $D_m$ ) was fitted in the model so

that the predicted values match with the experimental data. The fitted value of diffusivity for acetic acid-TBP case is  $6 \times 10^{-11}$  m<sup>2</sup>/s. This value has been used for remaining sets of predictions for acetic acid-TBP system. The similar procedure was applied here for the formic acid and phenylacetic acid predictions.

Model simulation data was used here to understand the variation of interfacial concentrations and distribution coefficients with time (Fig. 3b). Figure 3b shows the relationship between interfacial concentrations ( $C_{if}$  and  $C_{imf}$ ), distribution coefficient ( $k$ ) and time. An decrease in feed side acid concentrations ( $C_{if}$ ) at feed-membrane interface has been observed with an increase in time. The decrease was due to the depletion of acid concentration from the bulk of the feed phase. According to Eq. (15), the reaction equilibrium shifted towards reduced formation of acid-complex. As a result, the complexation of TBP reduced and hence  $C_{imf}$  decreased with time. Formation of acid complex occurred at the feed-membrane interface. The acid complex then diffused through the membrane phase. Continuous increase in  $k$  was observed with time (Fig. 3b). The rate of decrease in  $C_{if}$  was higher in comparison to  $C_{imf}$  at any given time. As a result, there was a rapid increase in  $k$ . High values of  $k$  led to increase in overall mass transfer coefficient ( $K$ ). Ultimately, higher values of  $C_{imf}$  contributed to the higher mass transfer flux.



### Effect of initial concentrations of carboxylic acid

This study was performed with various initial concentrations (0.05, 0.3 and 0.5M) of acetic acid in feed. The relationship between percent transport of acetic acid and time was studied. It can be seen that the model predictions are in good agreement with the experimental observations. The percent transport obtained for the case with low acid concentration (0.05M) was higher compared to high acid concentrations (0.3 and 0.5M). In comparison with high acid concentrations feed, the number of acid molecules available in low acid concentration feed were less. Thus, more numbers of extractant molecules were available for making complex with acid molecules at low acid concentrations compared to at high acid concentrations. As a result the percent transport for low acid concentration was obtained higher compared to high acid concentrations.

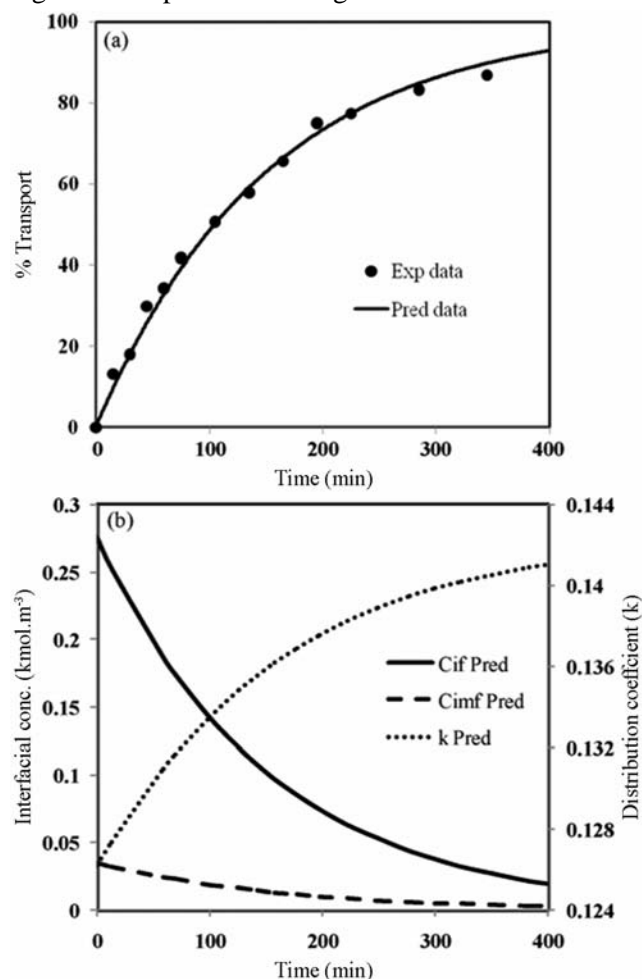


Fig. 3 — Percent transport profiles for the base case (Feed phase, 0.3M acetic acid solutions (1000 mL); Organic phase, 10% (w/w) TBP in dodecane; Strip phase, 1M NaOH (500 mL); Feed / strip phase flow rates, 200 mL/min)

Therefore, the percent transports obtained for 0.05, 0.3 and 0.5M acetic acid with 10% TBP were 89.54, 86.91 and 82.72% respectively within 360 min.

### Effect of extractant concentration

Effect of extractant concentration on percent transport of carboxylic acid was studied using various concentrations (1-30% w/w) of TOA extractant. The relationship between percent transport of phenylacetic acid for different concentration of TOA and time. An increase in percent transport has been observed with increase in extractant concentrations. The initial flux values for 0.05M phenylacetic acid with 1, 5, 10 and 30% TOA extractant were  $13.18 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $41.55 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $48.53 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) and  $53.25 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) respectively. The fluxes calculated above 5% TOA extractant were nearly similar in values. Thus, percent transport values above 5% TOA concentration were almost similar for phenylacetic acid. The percent transport values for 0.05M phenylacetic acid with 1, 5, 10 and 30% TOA extractant were 67, 97, 99 and 99.6% respectively within 20 min. These are favorable results for the practical operation of phenylacetic acid extraction with amine based extractant (TOA). The flux value calculated for 30% TOA concentration is almost four times the value calculated for 1% TOA. Hence, it took longer to achieve 100% extraction with 1% TOA.

### Comparison of different carboxylic acids with organic extractant

The effect of different carboxylic acids on percent transport was studied using carboxylic acids such as acetic acid, formic acid and phenylacetic acid. TBP (1% w/w) extractant diluted with dodecane was used as organic phase in membrane. The relationship between percent transport of different carboxylic acids and time was studied. It can be seen that model predictions are in good agreement with the experimental observations. An increase in percent transport has been observed with time. The percent transport observed for phenylacetic acid was higher compared to formic acid and acetic acid. The initial flux values for acetic acid, formic acid and phenylacetic acid with 1% TBP concentration were  $1.022 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $1.002 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) and  $16.81 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) respectively (Table 4). The feed phase diffusivities ( $D$ ) of carboxylic acids have been calculated using Wilke-Chang correlation (Eq. (19)). The feed phase diffusivities of acetic acid, formic acid and phenylacetic acid were  $1.24 \times 10^{-9}$  m<sup>2</sup>/s,  $1.43 \times 10^{-9}$  m<sup>2</sup>/s and  $77.2 \times 10^{-9}$  m<sup>2</sup>/s respectively.

The fluxes and feed phase diffusivity for phenylacetic acid were much higher compared to formic acid and acetic acid. Therefore, the percent transport observed for phenylacetic acid was too high compared to formic acid and acetic acid. Similarly, the percent transport observed for formic acid was high compared to acetic acid due to its high diffusivity ( $D$ ). Thus, the percent transports observed for acetic acid, formic acid and phenylacetic acid were 11%, 24% and 97% respectively within 80 minutes.

#### Comparison of different organic extractants with carboxylic acid

The effect of different organic extractants on percent transport of carboxylic acid (HA) was studied using organic extractants such as TBP, TOA and TOPO. This study was performed with 0.05M phenylacetic acid. The plot between percent transport of phenylacetic acid (0.05M) with different organic extractants (TBP, TOA and TOPO) and time is shown in Fig. 4. Model predictions showed  $\pm 5\%$  error with experimental data. An increase in percent transport of phenylacetic acid has been observed with time. The percent transport for TOPO extractant was higher compared to TBP and TOA extractant. The detail description of carboxylic acid initial flux and membrane diffusivity for different organic extractants is shown in Table 4. The decreasing order of initial flux of phenylacetic acid with different organic extractant was observed as TOPO > TBP > TOA. Thus, the initial fluxes of phenylacetic acid for the extractant TBP, TOA and TOPO were  $16.81 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $13.18 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $39.42 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) respectively (Table 4). The flux obtained

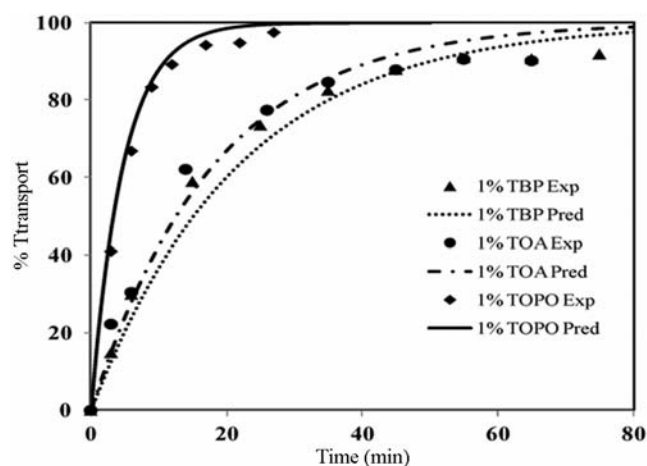


Fig. 4 — Comparison of different organic extractants (EXTs) (Feed phase, 0.05M phenylacetic acid solution (500 mL); Organic phase, 1 wt % EXTs solution; Strip phase, 1M NaOH (500 mL); Feed / strip phase flow rates, 200 mL/min)

for phenylacetic acid with TBP and TOA extractants does not show much difference. Therefore, the percent transport values observed from the experimental results for phenylacetic acid with TBP, TOA and TOPO extractants were 73%, 74% and 95% respectively within 25 mins. The membrane phase diffusivities of phenylacetic acid for TBP, TOA and TOPO extractants were  $0.9 \times 10^{-10}$  m<sup>2</sup>/s,  $2.2 \times 10^{-10}$  m<sup>2</sup>/s and  $6.0 \times 10^{-10}$  m<sup>2</sup>/s respectively. The flux and membrane phase diffusivity does not show any relation in this case with phenylacetic acid.

#### Effect of feed/strip flow rate

The effect of flow rate on percent transport of carboxylic acids was studied in hollow fiber supported liquid membrane module. This study was performed for 0.05 M phenylacetic acid and 1% TOPO as an extractant. The feed and strip flow rate was varied in the range of 50-500 mL/min. The result obtained from this study shows that the extent of carboxylic acid transport increases with an increase in flow rate. The percent transport observed for 50-100 mL/min flow rate was lower compared to 200-500 mL/min flow rate. The fluxes observed for phenylacetic acid with 50mL/min, 100 mL/min, 200 mL/min, 300mL/min and 500 mL/min were  $25.9 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $37.02 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $39.42 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr),  $49.5 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) and  $52.7 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) respectively. Therefore, the percent transport values observed for phenylacetic acid with 50mL/min, 100 mL/min, 200mL/min, 300mL/min and 500mL/min were 74, 89, 95, 97 and 98% respectively within 15 mins. The percent transport observed below 200mL/min showed significance difference. Beyond 200mL/min, there was not much change observed in percent transport. Therefore, all the experiments in the present work were carried out with optimized flow rate of 200mL/min.

#### Effect of feed volume

This study was performed at 1000 ml and 3000 ml feed volumes. The concentration of acetic acid was kept constant at 0.05M during this study. The initial flux values for acetic acid with 1000 mL and 3000 ml feed volumes were  $15.7 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) and  $16.7 \times 10^{-5}$  (kmol/m<sup>2</sup>.hr) respectively. Almost similar fluxes were obtained in both the cases. With increasing feed volume the numbers of moles of acetic acid in the feed phase increases. As a result, the time required for the transport of the acid molecules

from feed phase to strip phase increases with an increase in the feed volume. For 1000 mL feed volume, 98% transport was obtained in 200 min. But for 3000 mL feed volume, it took longer to achieve 98% transport. The simulation results were in good agreement with the experimental data.

#### Effect of scale up in HFSLM

The effect of scale up on carboxylic acid extraction was studied using acetic acid and TBP as an extractant. The relationship between percent left of acetic acid in feed reservoir with respect to different scale modules and time was studied. It can be seen that, model simulations are in good agreement with the experimental observations. Almost similar flux values were obtained for both the scale of modules. To achieve the say, 70% extraction of acetic acid, the large scale module required about 10 min, whereas the small scale module required about 40 min. This is because; larger module having six times membrane area compared to the small scale module.

#### Conclusion

The generalized methodology for carboxylic acids extraction (a) equilibrium study (b) transport behaviour and (c) scale up study has been proposed. The results obtained in this work have shown that carboxylic acids could be extracted using supported liquid membrane (SLM) technique. Equilibrium studies showed that TOPO is a better extractant for carboxylic acids extraction compared to TBP and TOA. This is because the higher basic strength of TOPO compared to TBP and TOA. Almost 99% extractions of carboxylic acids have been achieved using 1% TOPO within less time compared to other extractants. A mathematical model has been developed to predict the transport of carboxylic acids from feed to the strip side. The model predictions were reasonably good and the results showed that the effect of different process parameters could be essentially attributed to the percent transport of carboxylic acids. Scale-up experiment has shown that flux obtained at both scales is the same and hence the rate of extraction is significantly faster in a module with higher surface area. In other words, results scale with interfacial area.

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#### Nomenclature

- $C_{f0}$  Bulk concentration of the carboxylic acid in the feed reservoir or the bulk inlet concentration of the carboxylic acid in the feed-side (lumen-side) fluid at the fiber inlet, (kmol/m<sup>3</sup>)
- $C_f(0)$  Bulk concentration of the carboxylic acid in the feed reservoir at initial time ( $t = 0$ ), (kmol/m<sup>3</sup>)
- $C_f(t)$  Bulk concentration of the carboxylic acid in the feed reservoir at any time ( $t > 0$ ), (kmol/m<sup>3</sup>)
- $C_f$  Bulk concentration of the carboxylic acid in the feed-side (lumen-side) fluid at location 'z' of the fiber (kmol/m<sup>3</sup>)
- $C_{fz}$  Bulk outlet concentration of the carboxylic acid in the feed-side (lumen-side) fluid at the fiber exit (kmol/m<sup>3</sup>)
- $C_{if}$  Concentration of the carboxylic acid in the feed-side (lumen-side) fluid at feed-membrane interface (kmol/m<sup>3</sup>)
- $C_{imf}$  Concentration of the acid-extractant complex in the supported liquid (membrane-fluid) at feed-membrane interface (kmol/m<sup>3</sup>)
- $C_{ims}$  Concentration of the acid-extractant complex in the supported liquid (membrane-fluid) at strip-membrane interface (kmol/m<sup>3</sup>)
- $D$  Molecular diffusion coefficient of carboxylic acid in the aqueous phases, (m<sup>2</sup>/s)
- $D_m$  Molecular diffusion coefficient of acid-extractant complex in the supported liquid (m<sup>2</sup>/s)
- $K$  Overall mass transfer coefficient of carboxylic acid molecule (m/s)
- $k$  Predicted value of distribution coefficient of carboxylic acid (-)
- $k_d$  Experimental value of distribution coefficient of carboxylic acid (-)
- $K_{ex}$  Extraction Equilibrium constant of the acid complexation reaction (kmol<sup>-1</sup>.m<sup>3</sup>)
- $k_f$  Feed-side film mass transfer coefficient (m/s)
- $k_s$  Strip-side film mass transfer coefficient (m/s)
- $L$  Effective length of the hollow fiber module (m)
- $L_0$  Initial concentration of the extractant in the supported liquid (membrane phase) (kmol/m<sup>3</sup>)
- $M_B$  Molecular weight of solvent B (water)
- $N$  Total number of fibers in the module
- $Q_f$  Total volumetric flow rate of feed phase through lumen side of the module (m<sup>3</sup>/s)
- $Q_s$  Total volumetric flow rate of strip phase through shell side of the module (m<sup>3</sup>/s)
- $Q$  Permeate mass flow rate (kg/s)

- $r_{if}$  Inner radius of the hollow fiber tube (m)  
 $R_T$  Mass transfer flux of the carboxylic acid molecule (kmol / m<sup>2</sup>.s)  
 $R_{TCM}$  Mass transfer flux of the acid-extractant complex (kmol / m<sup>2</sup>.s)  
 $t$  time (min)  
 $T$  Temperature (K)  
 $u_f$  Velocity of feed phase through lumen side of the module (m/s)  
 $u_s$  Velocity of strip phase through shell side of the module (m/s)  
 $v_A$  Solute molal volume at normal boiling point (m<sup>3</sup>/kmol)  
 $V_f$  Fluid volume in the feed phase reservoir (m<sup>3</sup>)  
 $V_s$  Fluid volume in the strip phase reservoir (m<sup>3</sup>)  
 $\Delta P$  Applied pressure across the membrane (N/m<sup>2</sup>)  
 $d$  Membrane pore diameter ( $\mu$ m)  
 $\sigma$  Surface tension (N/m)  
 $d_0$  Membrane thickness (m)  
 $z$  Axial coordinate (m)  
 $\tau$  Tortusity of membrane (-)  
**Greek symbols**  
 $\varepsilon$  Porosity of the membranes  
 Contact angle (rad.)  
 $\rho$  Density of fluid (kg/m<sup>3</sup>)  
 $\mu$  Viscosity of fluid (kg/m.s)  
 $\varphi$  Association factor for solvent (-)

## References

- Helsel R, *Chem Eng Prog*, 73 (1977) 55.
- Jagirdar G C & Sharma M M, *J Sep Proc Technol*, 1 (1980) 40.
- Busche R M, Shimshick E J & Yates R A, *Biotechnol Bioeng Symp*, 12 (1982) 249.
- Tamada J A, Kertes A S & King C J, *Ind Eng Chem Res*, 29 (1990) 1319.
- Chand S & Jain S K, *Indian J Environ Prot*, 13 (1993) 761.
- Xing R, Qi W & Huber G W, *Energy Environ Sci*, 4 (2011) 2193.
- Kim S H, Yang J L & Song Y S, (1999) 40.
- Demiral H & Yildirim M E, *Water Sci Technol*, 47( 2003) 183.
- Saha B, Chopade S P & Mahajani S M, *Catal Today*, 60 (2000) 147.
- Golob J, Grllc V & Zadnik B, *Ind Eng Chem Process Des Dev*, 20 (1981) 433.
- Qin Y, Sheth J P & Sirkar K, *Ind Eng Chem Res*, 42 (2003) 582.
- Sheng J L, Huan L Chen & Zhang L, *Sep Purif Technol*, 66 (2009) 25.
- Basu R & Sirkar K, *AIChE J*, 37 (1991) 383.
- Narayanan J & Palanivelu K, *Ind J Chem Tech*, 15 (2008) 266.
- Kouki N, Tayeb R & Dhahbi M, *Desalin Water Treat*, 52 (2013) 4745.
- Prapasawat T, Lothongkum A W, & Pancharoen U, *Chem Pap*, 68 (2013) 180.
- Hao Z, Vilt M E, Wang Z, Zhang W & Winston W S Ho, *J Memb Sci*, 468 (2014) 423.
- Ansari S A, Mohapatra P K, Raut D R, Adya V C, Thulasidas S K & Manchanda V K, *Sep Purif Technol*, 63 (2008) 239.
- Pabby A K & Sastre A M, *J Memb Sci*, 430 (2013) 263.
- Rathore N S, Sonawane J V, Anil K, Venugopalan A K, Singh R K, Bajpai D & Shukla J, *J Memb Sci*, 189 (2001) 119.
- Ramakul P, Prapasawat T, Pancharoen U & Pattaveekongka W, *J Chinese Inst Chem Eng*, 38 (2007) 489.
- Norman N L, *AIChE J*, 17 (1969) 459.
- Parhi P K, *J Chem*, (2013) 1.
- Hong Y & Hong W, *Bioprocess Eng*, 22 (2000) 281.
- Hong Y, Hong W & Han D, *Biotechnol Bioprocess Eng*, 6 (2001) 386.
- Hong Y, Hong W H & Chang H N, *Biotechnol Letter*, 22 (2000) 871.
- Hano T, Mstumoto M, Hirata M & Miura S, *ISEC*, (1996) 1477.
- Solichien M, Brien D, Hammond E & Glatz C, *Enzyme Microb Technol*, 17 (1995) 23.
- Bird R, Stewart W & Lightfoot E, *Transport Phenomena*, 2<sup>nd</sup> ed, New York, (2000).
- Stokes J & Evans D, *Fundamental of Inerfacial Engineering*, 1<sup>st</sup> ed, New York, (1996).
- Vernekar P, Patwardhan A W, Patwardhan A V, Ansari S A, Mohapatra P K & Manchanda V K, *Chem Eng Res Des*, 91 (2013) 141.
- Vernekar P, Patwardhan A W, Patwardhan A V, Ansari S A, Mohapatra P K & Manchanda V K, *Sep Sci Technol*, 48 (2013) 1003.
- Yang M & Cussler E, *AIChE J*, 32 (1986) 1910.
- Wilke C & Chang P, *AIChE J*, 1 (1955) 264.
- Qader A, *M A Thesis Submitt. to Chem Eng Bradford, UK* (1991)
- Fahim M, Qader A & Hughes M, *Sep Sci Technol*, 27 (1992) 1809.
- Matsumoto M, Otono T & Kondo K, *Sep Purif Technol*, 24 (2001) 337.
- Wasewar K, Heesink A, Versteeg G & Pangarkar V, *J Chem Technol Biotechnol*, 77 (2002) 1068.
- Yang S, White S & Hsu S, *Ind Eng Chem Res*, 30 (1991) 1335.
- Rani K, Kumar T, Murthy J, Sankarshana T & Vishwanadham B, *Sep Sci Technol*, 45 (2010) 654.
- Wardell J & King C, *J Chem Eng Data*, 23 (1978) 144.