Mathematical model for swelling in a liquid emulsion membrane system

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Abstract

Application of the liquid emulsion membrane (LEM) technology to the industrial scale is hindered by the challenges imposed by stability of the emulsion during the transfer of the solute (pertraction). One of the important factors which leads to the instability is swelling. Emulsion undergoes swelling due to the osmotic gradient across the membrane as well as due to the occlusion of the external phase into the membrane phase; the latter is caused by the hydrodynamic deformation of the membrane globules. In the present work, we have studied swelling of the emulsion phase in a water-in-oil-in-water type LEM system. Nitric acid is the internal aqueous phase and is encapsulated in organic membrane phase composed of DEHPA–kerosene–SPAN80. Demineralised water is used as the external phase. The effect of the composition of the system and the hydrodynamic condition on the rate of swelling has been studied. A mathematical model has been developed to describe the effects of the relevant parameters on swelling of the emulsion. The globules of the emulsion are viewed as having a core-shell structure, based on the visual evidence. The model takes into account both the osmotic and the occlusion modes of swelling and also the leakage of the internal phase. The predictions of the model are found to be in good agreement with the experiments. The model would be useful for evaluating the rate of pertraction of a solute through the membrane–strip combination used in the present study. The study would also be useful for tuning the design and the operating parameters in LEM pertraction to achieve minimum swelling of the emulsion.

Keywords: Liquid emulsion membrane; Pertraction; Swelling; Osmosis; Occlusion
1. Introduction

Liquid emulsion membranes have demonstrated a considerable potential as effective tools for a wide variety of separations, especially from dilute solutions including hydrocarbon separation, mineral recovery, wastewater treatment, separation of toxic material like uranium and cadmium from effluents [1–4]. Boyadzhiev and Lazarova [5] have brought out the advantages of LEM over the conventional solvent extraction process in low solvent inventory, low equipment cost and higher mass transfer rate due to a larger available surface area for extraction. Bart et al. [6] have a cost comparison of extraction, permeation and precipitation. According to them, the LEM process is very promising for clean up of waste streams in view of rising dumping prices for hazardous sludge.

Application of LEM technology to industrial scale is, however, hindered by the challenges imposed by stability of the emulsion during pertraction. Swelling of emulsion, rupture of the globule and leakage of the internal phase into the external one are the major drawbacks of the process. Swelling in LEM is caused by the transfer of water from the external phase into the internal phase through the membrane by permeation and entrainment [7]. The stability of the emulsion drop decreases due to swelling and it becomes more prone to leakage and breakage [8]. Also, swelling of the emulsion dilutes the internal strip and lowers selectivity for separation. Nakashio et al. [9] have analyzed the reasons for very few industrial applications of LEM and emphasized the need for development of LEM with acceptably low level of swelling, high levels of stability and permeability and ease of demulsification, for complete solute recovery. Appropriate hydrodynamic conditions are necessary to generate a stable primary emulsion, which will resist swelling and rupture of the globules during pertraction. Again, too stable an emulsion will be difficult to demulsify, after pertraction, for the recovery of the product. Hence, a proper choice of the composition of the primary emulsion (viz. the carrier and the surfactant) is needed for formulating an emulsion, which is stable during pertraction, but could be easily destabilized after the solute recovery.

There are two modes of emulsion swelling, viz. occlusion swelling and osmotic swelling. In the occlusion or entrainment swelling, the external phase is occluded in the emulsion globule during pertraction. Agitation and presence of surfactant causes this type of swelling [10]. Ding and Xie [11] observed that various surfactants have different effects on occlusion and the choice of surfactant is important to reduce the rate of occlusion. Osmotic swelling or permeation swelling occurs when the solvent of the external phase diffuses in the emulsion globule due to the difference in the concentration of the solute between the internal and external aqueous phases.

Yan and Pal [12] have studied a primary emulsion drop under microscope and evaluated swelling and entrainment at various surfactant concentrations. Ramasedar et al. [13] have studied osmotic swelling, occlusion and breakage of emulsion. Several mechanisms have been suggested for permeation of water, viz. solute hydration [14], hydrated solute-carrier complexes and inverse micelles [15]. Colinert et al. [16] observed that the relative magnitude of two competitive effects caused by surfactants, viz. water hydration and membrane viscosity, is the basis for deciding the optimum surfactant concentration.

Usually, the LEM separation processes have been analyzed on the basis of the different configurations of the emulsion globule. Depending on the system under consideration, these can be divided into two general categories viz., the well-mixed internal phase model (also called core-shell/hollow sphere/membrane film model) and the rigid drop model (e.g., advancing front/shrinking core and reversible reaction model). The well-mixed internal phase model (Fig. 1) suits better to emulsion prepared at a low speed of agitation and/or in emulsion prepared with a low surfactant concentration so that the droplets of strip have
sufficient mobility for getting coalesced [17–20]. This model is simple in approach, involves a lower number of parameters and provides approximate estimates useful for preliminary design calculations.

Several authors [21–26] have worked on the basis of the concept that the internal droplets are rigidly embedded in the membrane phase of the primary emulsion globule (Fig. 2). The main difficulty with the rigid drop model is that it is not compatible with any physically relevant mechanisms of leakage. The actual situation, therefore, may fall between two extreme cases, one of the rigid drop and the other of the core-shell model.

Mathematical models for transport of water by osmosis have been presented by several authors [27–29]. Colinert et al. [16] have presented a model for swelling of globules using a core-shell type of structure for the globule. The model uses five parameters which have been estimated by experimental results. Three of these parameters are related to the characteristics of the surfactant used. The osmotic coefficient and membrane thickness are the other two parameters. Bart et al. [15] have presented a reaction front model in which osmosis occurs due to solubilization of water by inverse micelles diffusing through the organic membrane.

All the models reported in the literature are limited in their application because they either consider a single mode of swelling or else lump all the modes of swelling into a single swelling parameter. Since different modes of swelling/leakage have different dependences on the system parameters, it is necessary to account for these dependences separately in the model. This provides motivation for the present work.

For the present study a liquid emulsion membrane system composed of carrier–surfactant–diluent–strip combination of DEHPA–SPAN80–kerosene–nitric acid has been considered. This system has a high potential for the recovery of low concentration of uranium from a dilute nitrate solution as the raffinate stream of uranium refining. This work will be useful for generation of design data for this process.

2. Experimental

The set up consists of four parts viz. primary emulsifier, pertractor, phase separator and demulsifier. A schematic of the experimental set up is given in Fig. 3. The primary emulsifier and the pertractor were mechanically agitated contactors placed in a water bath with a temperature monitor. Demulsification was conducted thermally in a thermostatic bath heated with hot water. A thermometer was used to monitor the temperature.
Analytical grade di-2-ethylhexylphosphoric acid (DEHPA) (M/S Sigma Chemical Co.) was used as a carrier. The stripping agent, nitric acid (analytical grade), was obtained from M/S T.A. Corp., and kerosene, of commercial grade, was obtained from M/S IRE Ltd. India was used as diluent for the carrier. The surfactant SPAN 80 was obtained from M/s Mohini Organics.

The liquid membrane phase was prepared by mixing the organic carrier and the surfactant in the organic diluent in the primary emulsifier at speed of 100 rpm. The primary emulsion was then
formed by adding an equal volume of the strip solution to the liquid membrane phase in a dropwise manner while agitating the membrane phase at a high speed (3000 rpm). The addition was completed in around 20 min. The mixture was then cooled to room temperature.

The pertraction was conducted in the pertractor. The treat ratio, i.e., the ratio of the feed (DM water in this study) to the primary emulsion (organic) was kept at 10 : 1 in most cases. The measured quantity of the feed solution was taken in the pertractor and the primary emulsion was added slowly, under agitation (300 rpm). The temperature during the pertraction was maintained at 28°C. The samples were withdrawn periodically from the aqueous phase, filtered and analyzed for the acidity. In the lower range, acidity was measured with a digital pH meter (Equiptronics EQ610). A higher range of acidity was measured by acid base titration using standard alkali (sodium hydroxide) and phenolphthalein indicator.

Settling of the secondary emulsion generated during the pertraction step was done in a 500 ml glass separating funnels. A settling time of 10 min was maintained in all the experiments. Swelling was estimated by measuring the volume of the primary emulsion after phase separation following pertraction, and comparing it with the volume of the primary emulsion before pertraction.

Studies on stability of the primary emulsion composed of DEHPA (1% v/v)–SPAN80–kerosene–HNO₃ (2 M with 50% v/v loading) and measurement of the size of the emulsion globules was done by capturing images of the globules with an image capturing system. It consisted of a CCD camera, a frame grabber card with 25 frame/s capturing speed, an optical microscope and an image analysis software (Fig. 2). For capturing images of the emulsion globule under microscope, a tiny drop of the primary emulsion was put into a watch glass containing DM water and a single globule was focused. The water taken in the watch glass contained TWEEN80 (20% v/v) to prevent coalescence of the globule. Thus, a water in oil in water (W/O/W) type double emulsion was formed with a globule of the primary emulsion (W/O) in a pool of water. Images of the globule were captured at various intervals of time to observe the fate of the internal droplets. Measurement of the average size of the globules was done online while agitating a small volume of the primary emulsion in the aqueous feed solution at various speeds of pertraction using the image capturing system.

3. Mathematical model

Figs. 4 and 5 show the images of the primary emulsion prepared with 3% and 5% surfactant (SPAN80) concentration respectively with the stirrer speed of 3000 rpm. For higher concentration of the surfactant, the internal droplets appear to be more stable resembling a rigid drop. Since in the present set of experiments only 3% surfactant is used (for ease of demulsification), there is ground to believe that there will be a substantial circulation of the droplets inside the emulsion globules and also a significant coalescence. The photograph of emulsion used in this work (Fig. 4) supports this fact. This finding favors the shell and core model rather than the rigid drop model.

The relevant model for the process of swelling by occlusion and osmosis and leakage is developed below. The following assumptions are made in the development of the model.

(i) A globule is viewed as a sphere. The internal phase is assumed to form a spherical core. It is surrounded by the membrane layer in the form of a shell (Fig. 2).

(ii) The external mass transfer resistance of the globule is neglected. This is a reasonable assumption in view of the fact that the membrane thickness (about 25 μm) is much larger than the external diffusion film thickness (about 5 μm). Moreover, the viscosity of the membrane fluid is much higher than that of the external fluid. Hence most of the mass transfer resistance will be located inside the membrane.
(iii) The volume of the internal phase changes with time due to occlusion of the external phase and the leakage of the internal phase. The volume of the membrane phase, however, is assumed to remain constant. This results in a variation of the membrane thickness with time. This affects both the rate of occlusion as well as leakage.

(iv) Occlusion occurs due to deformation of the membrane. This deformation results in formation of cavities, which occlude the external phase. Deformability of the membrane and hence the rate of occlusion should increase with the increase in the thickness of the membrane. The rate of occlusion is assumed to be directly proportional to the thickness of the membrane and the outer surface area of the globule. Hence it could be written as

\[ r_o = k_o \left( \frac{t}{t_0} \right) A \]  

where \( r_o \) = volumetric rate of occlusion of the internal phase, \( k_o \) = the occlusion coefficient, \( t \) = thickness of the membrane, \( t_0 \) = the initial thickness of the membrane, and \( A \) = outer surface area of the globule. Note that both \( t \) and \( A \) vary with time.

(v) Leakage occurs due to rupture of the membrane. The thinner the membrane is, the more is the likelihood of it being ruptured. Based on this understanding, the rate of leakage is assumed to be inversely proportional to the thickness of the membrane and is written as

\[ r_l = k_l \left( \frac{t_0}{t} \right) A \]  

where \( r_l \) = volumetric rate of leakage of the internal phase, and \( k_l \) = leakage coefficient.

(vi) The internal phase is assumed to be completely mixed, on the other hand, the membrane phase is assumed to be unmixed.

(vii) In the case of nitric acid/DEHPA/water system, water is assumed to permeate (apart from
occlusion) into the globule by osmosis which is generated due to the difference in the concentration of the nitric acid in the internal and the external phases. The permeation is in the inward direction due to the higher concentration of HNO$_3$ in the internal phase.

The extent of swelling ($\psi_s$) of the emulsion globule and the extent of leakage of the internal phase ($p$) are given by the following equations (see mathematical model derived in the Appendix):

$$\frac{d\psi_s}{d\theta} = \left(\frac{3}{R^0}\right)^{2/3} \psi_s^{2/3} \left\{ p - p^e - \frac{1}{T_r} \left[ 1 - \frac{(\psi_s - \phi_m)}{(1 - \phi_m)} p \right] \right\}$$

$$+ k_a \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right)$$

$$- k_r \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (\phi_m)} \right)^{-1} \right\}$$

$$\frac{dp}{d\theta} = -\left(\frac{3}{R^0}\right)^{2/3} \left(\frac{\psi_s^{2/3}}{\psi_s - \phi_m} \right) \left\{ p - p^e - \frac{1}{T_r} \left[ 1 - \frac{(\psi_s - \phi_m)}{(1 - \phi_m)} p \right] \right\}$$

$$\left[ 1 - \frac{(\psi_s - \phi_m)}{(1 - \phi_m)} p \right] \left[ k_p \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right)^{-1} \right]$$

$$+ k_a \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right)$$

These two simultaneous ordinary differential equations have been solved using the fourth order Runge–Kutta method to obtain $\psi_s$ and $p$ as functions of time. The procedure for finding the values of the coefficients $k_a$, $k_r$ and $k_p$ is also given in the Appendix.

The above equations assume a simpler form for O/W/O double emulsion system, in which water as the internal phase is emulsified in the organic membrane phase which, again, is dispersed in the external water phase. Hence it is called water/membrane/water system. Here, swelling occurs only by occlusion. Since there is no nitric acid in the internal phase, there is no osmotic gradient across the organic membrane. The first term associated with the osmotic coefficient $k_0$ can be ignored and hence the reduced form of the expression for the rate of swelling is

$$\frac{d\psi_s}{d\theta} = \left(\frac{3}{R^0}\right)^{2/3} \psi_s^{2/3} \left\{ k_a \left[ \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right] \right\}$$

$$- k_r \left[ \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right]^{-1} \right\}$$

At time $\theta = 0$, Eq. (3) reduces to

$$\frac{d\psi_s}{d\theta} \bigg|_{\theta=0} = \left(\frac{3}{R^0}\right)(k_a - k_r)$$

Thus the initial slope gives the difference $k_a - k_r$. Also at steady state, Eq. (3) reduces to

$$\frac{k_a}{k_r} = \left[ \frac{1 - (1 - \phi_m)^{1/3}}{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}} \right]^{-2} \right\}$$

The two equations (4) and (5) could, in principle, be used to estimate the occlusion and the leakage coefficients.

4. Results and discussion

In this section, we first describe the experiments corresponding to the water/membrane/water system. The aim of these experiments is to
obtain both the leakage and the occlusion coefficients. Next we describe the experiments corresponding to nitric acid/membrane/nitric acid experiments. For correlating the results of these experiments, the values of the coefficients obtained from the water/membrane/water system are used.

Fig. 6 shows a plot of $\psi_s$ vs. $\theta$ in the water/membrane/water emulsion system at a stirrer speed of 300 rpm. The concentrations of the surfactant and the carrier are listed in the figure. The value of the slope of the plot for 300 rpm is $7.9 \times 10^{-4}$ s$^{-1}$. The average initial radius of the globules was measured to be $5.8 \times 10^{-5}$ m. From these values, the difference $k_a - k_i$ was calculated to be $1.5 \times 10^{-8}$ m.s$^{-1}$ [see Eq. (37A)]. It was not possible to separate the two coefficients using Eq. (35A) since it required attainment of the steady state. It was found that beyond 800 s, the globules became sticky and phase separation, after pertraction, was difficult. This introduced unacceptable inaccuracies in the measurement of the extent of swelling. However, independent measurement [30] gave the value of the leakage coefficient of $k_i = 1.50 \times 10^{-9}$ m.s$^{-1}$, which was an order of magnitude lower than $k_a - k_i$. Hence we assigned the value of $1.5 \times 10^{-8}$ m.s$^{-1}$ entirely to $k_i$.

The experiments were conducted at three different stirrer speeds (viz. 200, 300 and 500 rpm) but with the same values of the membrane composition. All of them yielded the same value of $k_a$ of $1.5 \times 10^{-8}$ m.s$^{-1}$. Microscopic measurements of the average globule size at various rpm during pertraction are given in Table 1. The size decreases with the increase in the agitator speed as expected. The increase in the intensity of agitation will tend to induce a greater extent of deformation of globules. On the other hand, the smaller size will render the globules more resistant to deformation. It appears from the results of these experiments that the effect of the intensity of agitation on deformation of the globules is counterbalanced by a greater rigidity of smaller globules.

There is a small but significant influence of the surfactant concentration on the occlusion co-

![Fig. 6. Extent of occlusion in W/M/W emulsion at various impeller speeds, $N_p$ rpm. The solid lines are model fit and the symbols are experimental data. Ratio of volume of external to membrane phase = 10, initial concentration of DEHPA in the membrane = 30 mol/m$^3$, concentration of SPAN80 in the membrane = 69 mol/m$^3$; speed of pertraction = 300 rpm, speed of emulsification = 3000 rpm, parameters: $k_a = 1.5 \times 10^{-8}$ m.s$^{-1}$, $k_i = 1.5 \times 10^{-9}$ m.s$^{-1}$.](image-url)
efficient as is evident from Fig. 7. The values of the coefficients obtained by regression are given in Table 2. The leakage coefficient values have been obtained from independent experiments [30]. It is observed that with an increase in the concentration of SPAN80, there is an increase in the magnitude of the occlusion coefficient and decrease in the values of the leakage coefficient. This trend is expected because the increase in surfactant will result in the decrease in the interfacial tension of the membrane making it more deformable. This will promote occlusion of the external phase into the membrane. Viscosity of membrane increases with the increase in the concentration of the surfactant. This reduces the internal circulation and escape of droplets and hence, the leakage coefficient.

Table 1
Average globule size measured photographically at various pertraction speeds, $N_p$

<table>
<thead>
<tr>
<th>$N_p$, rpm</th>
<th>$R_0 \times 10^5$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>7.5</td>
</tr>
<tr>
<td>300</td>
<td>5.8</td>
</tr>
<tr>
<td>500</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 2
Model parameters ($k_a$ and $k_z$) obtained by regression for various surfactant concentrations $[S]$ in the water/membrane/water system

<table>
<thead>
<tr>
<th>$[S]$ mol.m$^{-3}$</th>
<th>$k_a \times 10^8$ m.s$^{-1}$</th>
<th>$k_z \times 10^9$ ms$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1.38</td>
<td>1.71</td>
</tr>
<tr>
<td>46</td>
<td>1.43</td>
<td>1.62</td>
</tr>
<tr>
<td>69</td>
<td>1.50</td>
<td>1.50</td>
</tr>
</tbody>
</table>

*These values have been obtained from independent experiments [30]

Fig. 7. Extent of occlusion in W/M/W emulsion for various concentrations of the surfactant $[S]$, mol/m$^3$. The solid lines represented by A, B and C are the model fits and the symbols are the experimental data. ● = 23 mol.m$^{-3}$ (A), ▲ = 46 mol.m$^{-3}$ (B), ▲ = 69 mol.m$^{-3}$ (C); treat ratio = 10, speed of pertraction = 300 rpm ($R_0 = 5.8 \times 10^5$ m), initial concentration of DEHPA in the membrane = 30 mol/m$^3$, concentration of SPAN80 in the membrane = 69 mol/m$^3$, speed of emulsification = 3000 rpm. The model parameter values obtained by regression are given in Table 2.
The experiments for studies on osmotic swelling were conducted with concentrated nitric acid in the strip phase and water in the external phase. The leakage of the nitric acid into the external phase was monitored by measurement of acidity of the external phase. The rate of swelling at three different impeller speeds is presented in Fig. 8. For fitting the experimental data, the previously obtained (during W/M/W experiments) values of $k_a$ and $k_i$ have been used. Only the values of $k_p$ have been estimated by regression of these plots. It is important to note that a single set of values of $k_a$, $k_i$ and $k_p$ could fit data for all three speeds of agitation. Insensitivity of $k_p$ to agitation speed is consistent with the corresponding insensitivity of $k_a$, $k_i$ and it stems from the fact that smaller size globules resist the increased deformation at a higher impeller speed.

The data on the extent of swelling of the emulsion for various concentrations of nitric acid in the internal phase (strip) are presented in Fig. 9. The same set of the parameters as used in Fig. 8 can fit all the curves. This is a strong evidence of the validity of the present model.

Fig. 10 presents the effect of the concentration of the surfactant on the extent of swelling. The regression estimates of the parameters are presented in Table 3. It is important to note that the same set of occlusion and leakage coefficient values which were used in Fig. 6 have also been used here. Only the osmotic coefficient has been regressed. The value of the osmotic coefficient decreases with the increase in the surfactant concentration. This is attributed to the increase in the membrane viscosity with the increase in the surfactant concentration.

Fig. 11 plots the extent of swelling of the emulsion as a function of the intensity of agitation during emulsification. The values of all the three coefficients decrease with the increase in the speed of emulsification (Table 4). The photographic studies presented earlier in this chapter can be

![Fig. 8. Extent of swelling as a function of the impeller speed, $N_p$, rpm. The solid lines represented by A, B and C are the model fits and the symbols are the experimental data. □ = 500 rpm (A), ▲ = 300 rpm (B), ● = 200 rpm (C). Treat ratio = ratio of volume of external to membrane phase =10, initial concentration of DEHPA in the membrane = 30 mol/m³, concentration of SPAN80 in the membrane = 69 mol/m³, concentration of nitric acid in the strip = 2000 mol/m³, speed of emulsification = 3000 rpm. Parameters: $k_a = 1.5 \times 10^{-8}$ m.s⁻¹, $k_i = 1.5 \times 10^{-9}$ m.s⁻¹, $k_p = 1.0 \times 10^{-8}$ m⁴.mol⁻¹.s⁻¹.](image-url)
Fig. 9. Extent of swelling as a function of initial concentration of strip, $[\text{HNO}_3]^i$, mol.m$^{-3}$. The solid lines represented by A, B and C are the model fits and the symbols are the experimental data. □ = 4000 mol.m$^{-3}$ (A), ▲ = 2000 mol.m$^{-3}$ (B), ● = 1000 mol.m$^{-3}$ (C). Treat ratio = ratio of the volume of the external to the membrane phase = 10, speed of pertraction = 300 rpm ($R^0 = 5.8 \times 10^{-5}$ m), initial concentration of DEHPA in the membrane = 30 mol/m$^3$, concentration of SPAN80 in the membrane = 69 mol/m$^3$, speed of emulsification = 3000 rpm. Parameters: $k_a = 1.5 \times 10^{-8}$ m.s$^{-1}$, $k_A = 1.5 \times 10^{-9}$ m.s$^{-1}$, $k_p = 1.0 \times 10^{-8}$ m$^4$.mol$^{-1}$s$^{-1}$.

Fig. 10. Extent of swelling as a function of the surfactant concentration, $[S]$ mol.m$^{-3}$. The solid lines represented by A, B and C are the model fits and the symbols are the experimental data. ● = 23 mol.m$^{-3}$ (A), □ = 46 mol.m$^{-3}$ (B), ▲ = 69 mol.m$^{-3}$ (C). Treat ratio = ratio of the volume of the external to membrane phase = 10, speed of pertraction = 300 rpm ($R^0 = 5.8 \times 10^{-5}$ m), initial concentration of DEHPA in the membrane = 30 mol/m$^3$, initial concentration of nitric acid in the strip = 2000 mol/m$^3$, speed of emulsification = 3000 rpm. The model parameter values obtained by regression are given in Table 3.
referred to explain this case. When the emulsion is prepared at a high speed of agitation \((N_e)\), the strip phase is finely dispersed and rigidly embedded in the membrane. In the framework of the core shell model, this implies that the shell becomes more rigid with the increase in the impeller speed during emulsification. The membrane

Table 3
Model parameters \((k_a, k_i, k_p)\) obtained by regression for various surfactant concentrations \([S]\) in the nitric acid/membrane/water system

<table>
<thead>
<tr>
<th>[S] mol.m(^{-3})</th>
<th>(k_a \times 10^8 \text{ m.s}^{-1})</th>
<th>(k_i \times 10^9 \text{ ms}^{-1})</th>
<th>(k_p \times 10^8 \text{ m}^4.\text{mol}^{-1}.\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
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</tr>
<tr>
<td>69</td>
<td>1.50</td>
<td>1.50</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 4
Model parameters \((k_a, k_i, k_p)\) obtained by regression for various speeds of emulsification \((N_e)\) for the nitric acid/membrane/water system

<table>
<thead>
<tr>
<th>(N_e) rpm</th>
<th>(k_a \times 10^8 \text{ m.s}^{-1})</th>
<th>(k_i \times 10^9 \text{ ms}^{-1})</th>
<th>(k_p \times 10^8 \text{ m}^4.\text{mol}^{-1}.\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>2.00</td>
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<td>1.50</td>
<td>1.50</td>
<td>1.00</td>
</tr>
<tr>
<td>5000</td>
<td>1.00</td>
<td>0.60</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* These values have been obtained from independent experiments [30]

is thus more resistant to deformation and hence all the coefficients decrease.

Comparing Figs. 8–11 with Figs. 6 and 7, we see that swelling in the presence of nitric acid in the strip phase is considerably higher than in its absence. This indicates that in the presence nitric

![Fig. 11. Extent of swelling of the membrane as a function of intensity of agitation during emulsification, \(N_e\), rpm. The solid lines represented by A, B and C are the model fits and the symbols are the experimental data. • \(N_e = 2000\) rpm (A), ▲ \(N_e = 3000\) rpm (B), □ = 5000 rpm (C). Treat ratio = ratio of the volume of the external to membrane phase = 10, speed of pertraction = 300 rpm \((R^0 = 5.8 \times 10^{-2} \text{ m})\), initial concentration of DEHPA in the membrane = 30 mol/m\(^3\), concentration of SPAN80 in the membrane = 69 mol/m\(^3\), initial concentration of nitric acid in the strip = 2000 mol/m\(^3\). The model parameter values obtained by regression are given in Table 4.](image-url)
acid, osmosis is a dominant mechanism of the swelling. This is also evident from the fact that 
\[ k_p^0 = k_p [\text{HNO}_3]^0 \] is three orders of magnitude higher than the occlusion coefficient. This is understandable since the nitric acid concentrations used in these experiments are very high.

5. Conclusions

The model presented in this work appears to be consistent with all the experimental data on both water/membrane/water system and nitric acid/membrane/water system under various operating conditions. The model is therefore a fairly good presentation of the actual process. The work has resulted in the following understandings about the LEM system.

1. For the present experiments, core and shell model appears to be appropriate representation of the emulsion globule.
2. The occlusion coefficient is independent of the impeller speed, which is consistent with the decrease in the globule size.
3. The occlusion coefficient increases with the increase in the surfactant concentration.
4. It is observed that between the two swelling mechanisms viz. occlusion and osmotic swelling, the latter dominates the rate.

The present study has allowed us to collect the information, which will be useful for estimating the rate of pertraction of a solute through the nitric acid/membrane/solution LEM system with the help of the developed model. The study will also provide data for tuning the design and the operating parameters in LEM pertraction to achieve minimum swelling of the emulsion. More importantly, it also provides an insight into the mechanisms of swelling and their relative importance.

Symbols

- \( A \) — Surface area of globule, m²
- \([D]\) — Concentration of DEHPA, mol/m³
- \([H]\) — Concentration of nitric acid, mol/m³
- \( k \) — Occlusion coefficient, m⁻¹
- \( k_p^0 \) — Occlusion coefficient, m⁴.mol⁻¹.s⁻¹
- \( k_p^0 \) — Osmotic coefficient, m.s⁻¹
- \( N_e \) — Impeller speed during emulsification, rpm
- \( N_p \) — Impeller speed during pertraction, rpm
- \([S]\) — Concentration of surfactant (SPAN80), mol/m³
- \( R \) — Radius of emulsion globule, m
- \( r_a \) — Volume rate of occlusion, m³.s⁻¹
- \( r_f \) — Volume rate of leakage, m³.s⁻¹
- \( r_p \) — Volume rate of osmosis, m³.s⁻¹
- \( t \) — Thickness of the membrane in the globule, m
- \( \text{TR} \) — Treat ratio = ratio of volume of external (feed) phase to emulsion phase
- \( T_r \) — Volume ratio of external to internal (strip) phase
- \( V \) — Volume, m³
- \( W/M/W \) — Water in membrane (oil) in water type double emulsion
- \( W/O \) — Water in oil type emulsion

Greek

- \( \phi_m \) — Membrane to acid phase ratio in the primary emulsion
- \( \theta \) — Time, s
- \( \psi \) — Ratio of the emulsion globule volume to its initial volume

Subscripts and superscripts

- \( e \) — External phase
- \( i \) — Internal phase
- \( m \) — Membrane phase
- \( 0 \) — Initial condition (time = 0)

Abbreviations

- DEHPA — Di(2ethylhexyl)phosphoric acid
- HNO₃ — Nitric acid
- LEM — Liquid emulsion membrane
- SPAN80 — Sorbitanmonooleate
TWEEN80 — Polyoxyethylene sorbitan mono-oleate

References

Appendix

Mathematical model

The rate of permeation of water into a globule is written using van’t Hoff rule as,

\[ r_p = k_p \left( \frac{t^0}{t} \right) A \left( [\text{HNO}_3]_i - [\text{HNO}_3]_e \right) \]  

(3A)

where \( k_p \) = osmotic or permeation coefficient, \( r_p \) = rate of permeation of water into the globule. The osmotic coefficient is assumed to be independent of the concentration of \( \text{HNO}_3 \).

Since the change of the volume, \( V \), of the globule is due to the change in the volume of the internal phase alone, the volume balance on a globule at any time \( \theta \) can be written, using Eqs. (1A)–(3A) as

\[ \frac{dV}{d\theta} = k_p A \left( \frac{t^0}{t} \right) \left( [\text{HNO}_3]_i - [\text{HNO}_3]_e \right) - k_i A \left( \frac{t^0}{t} \right) + k_a A \left( \frac{t}{t^0} \right) \]  

(4A)

Expressing the thickness of the membrane as the difference between the outer radius \( R \) and the inner radius \( R_i \) of the membrane, i.e.

\[ t = R - R_i \quad \text{and} \quad t^0 = R^0 - R_i^0 \]  

(5A)

we get

\[ \frac{t}{t^0} = \frac{R - R_i}{R^0 - R_i^0} \]  

(6A)

We denote the extent of swelling of the globule as

\[ \psi_s = \frac{V}{V^0} \]  

(7A)

Eq. (4A) can now be written in terms of the extent of swelling as follows:

\[ \frac{d\psi_s}{d\theta} = \frac{A}{V^0} \left[ k_p \left( \frac{t}{t^0} \right)^{-1} \left( [\text{HNO}_3]_i - [\text{HNO}_3]_e \right) + k_a \left( \frac{t}{t^0} \right)^{-1} \right] \]  

(8A)

We also define the ratio of the volume of the membrane phase to the initial volume of the globule as

\[ \phi_m = \frac{V_m}{V^0} \]  

(9A)

Note that

\[ R_i = \left( \frac{3}{4\pi} V_i \right)^{1/3} = \left( \frac{3}{4\pi} (V - V_m) \right)^{1/3} \]  

(10A)

Using Eqs. (7A) and (9A) we can rewrite the above equation as follows:

\[ R_i = R^0 \left( \psi_s - \phi_m \right)^{1/3} \]  

(11A)

At \( \theta = 0 \), \( \psi_s = 1 \) and Eq. (11A) reduces to

\[ R_i^0 = R^0 \left( 1 - \phi_m \right)^{1/3} \]  

(12A)

Using Eqs. (11A) and (12A), we can write

\[ \frac{t}{t^0} = \frac{R - R_i}{R^0 - R_i^0} = \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \]  

(13A)

At the steady state, i.e., at \( \theta = \infty \), \( t = t^\infty \) and \( \psi_s = \psi_s^\infty \), and hence

\[ \frac{t^\infty}{t^0} = \frac{R^\infty - R_i}{R^0 - R_i^0} = \frac{\psi_s^{\infty^{1/3}} - (\psi_s^\infty - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \]  

(14A)

The globule surface area \( A \) is related to its initial volume by the following equation:
\[
\frac{A}{\nu^0} = (36\pi^{1/3}) \left( \frac{V}{\nu^0} \right)^{2/3} \left( \frac{1}{\nu^0} \right)^{1/3}
\]
\[
= \left( \frac{3}{R_0} \right)^{2/3} \left( \psi_s \right)^{2/3}
\tag{15A}
\]

Eq. (8A) can now be modified using Eq. (15A) as follows:

\[
\frac{d\psi_s}{d\theta} = \left( \frac{3}{R_0^0} \right)^{2/3} \psi_s \left[ k_p \left( \frac{t}{t_0^0} \right)^{-1} ([\text{HNO}_3]_i - [\text{HNO}_3]_e) + k_a \left( \frac{t}{t_0^0} \right) - k_i \left( \frac{t}{t_0^0} \right)^{-1} \right]
\tag{16A}
\]

The mass balance of HNO$_3$ on a globule yields

\[
- \frac{d}{d\theta} ([\text{HNO}_3]_i V_i) = k_i \left( \frac{t_0^0}{t} \right) A [\text{HNO}_3]_i - k_a \left( \frac{t_0^0}{t} \right) A [\text{HNO}_3]_e
\tag{17A}
\]

Defining

\[
[\text{HNO}_3]_i^0 = p \quad \text{and} \quad [\text{HNO}_3]_e^0 = p_e
\tag{18A}
\]

and noting that

\[
V_i = V_i^0 (\psi_s - \phi_m)
\tag{19A}
\]

we can rewrite Eq. (17A) as:

\[
\frac{d}{d\theta} \left[ p (\psi_s - \phi_m) \right] = \left( \frac{3}{R_0^0} \right)^{2/3} \psi_s \left[ k_p \left( \frac{t}{t_0^0} \right)^{-1} \left( p - p_e \right) \right] + k_a \left( \frac{t}{t_0^0} \right) - k_i \left( \frac{t}{t_0^0} \right)^{-1}
\tag{20A}
\]

We can modify also modify Eq. (16A) as follows:

\[
\frac{d\psi_s}{d\theta} = \left( \frac{3}{R_0^0} \right)^{2/3} \psi_s \left[ k_p \left( \frac{t}{t_0^0} \right)^{-1} \left( p - p_e \right) \right]
\tag{21A}
\]

where

\[
k^0_p = k_p \left[ \text{HNO}_3 \right]^0
\tag{22A}
\]

Multiplying Eq. (21A) by \( p \) and subtracting it from Eq. (20A), we obtain

\[
- (\psi_s - \phi_m) \frac{dp}{d\theta} = \left( \frac{3}{R_0^0} \right)^{2/3} \psi_s \left[ p - p_e \right] + k_p \left( \frac{t}{t_0^0} \right)^{-1} \left( p + k_a \left( \frac{t}{t_0^0} \right) \right]
\tag{23A}
\]

Due to leakage, the concentration of nitric acid in the external phase changes with time. The variation of this concentration with time can be obtained from the following equation based on the balance of the nitric acid:

\[
V_i \left( [\text{HNO}_3]_e - [\text{HNO}_3]_{i0} \right)
= V_i^0 [\text{HNO}_3]_{i0} - V_i [\text{HNO}_3]_e
\tag{24A}
\]

In the above equation, \( V_i \) represents the volume of the external phase. It is assumed to be constant. Denoting the ratio of volume of external phase to the internal phase \( T_r \) as

\[
T_r = \frac{V_i}{V_i^0}
\tag{25A}
\]

We can rewrite Eq. (24A) as:

\[
p_e = p_e^0 + \frac{1}{T_r} \left[ 1 - \left( \psi_s - \phi_m \right) \right] p_e \tag{26A}
\]

\[
\left( \frac{3}{R_0^0} \right)^{2/3} \psi_s \left[ k_p \left( \frac{t}{t_0^0} \right)^{-1} \left( p - p_e \right) \right]
\tag{21A}
\]

where

\[
k^0_p = k_p \left[ \text{HNO}_3 \right]^0
\tag{22A}
\]

Multiplying Eq. (21A) by \( p \) and subtracting it from Eq. (20A), we obtain

\[
- (\psi_s - \phi_m) \frac{dp}{d\theta} = \left( \frac{3}{R_0^0} \right)^{2/3} \psi_s \left[ p - p_e \right] + k_p \left( \frac{t}{t_0^0} \right)^{-1} \left( p + k_a \left( \frac{t}{t_0^0} \right) \right]
\tag{23A}
\]

Due to leakage, the concentration of nitric acid in the external phase changes with time. The variation of this concentration with time can be obtained from the following equation based on the balance of the nitric acid:

\[
V_i \left( [\text{HNO}_3]_e - [\text{HNO}_3]_{i0} \right)
= V_i^0 [\text{HNO}_3]_{i0} - V_i [\text{HNO}_3]_e
\tag{24A}
\]

In the above equation, \( V_i \) represents the volume of the external phase. It is assumed to be constant. Denoting the ratio of volume of external phase to the internal phase \( T_r \) as

\[
T_r = \frac{V_i}{V_i^0}
\tag{25A}
\]

We can rewrite Eq. (24A) as:

\[
p_e = p_e^0 + \frac{1}{T_r} \left[ 1 - \left( \psi_s - \phi_m \right) \right] p_e \tag{26A}
\]
Substituting for \(p_s\) from the above equation into Eqs. (21A) and (23A) respectively, we obtain

\[
\frac{d\psi_s}{d\theta} = \left( \frac{3}{R^0} \right) \psi_s^{2/3} \left[ k_p^0 \left( \frac{t}{t^0} \right)^{-1} \left\{ p - p_c^0 - \frac{1}{T_r} \right\} + \left( \frac{\psi_s - \phi_m}{(1 - \phi_m)} \right) p \right] + k_a \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right) \]  

(27A)

\[
-(\psi_s - \phi_m) \frac{dp}{d\theta} = \left( \frac{3}{R^0} \right) \psi_s^{2/3} \left\{ p - p_c^0 - \frac{1}{T_r} \right\} \left[ 1 - \left( \frac{\psi_s - \phi_m}{(1 - \phi_m)} \right) p \right] + k_a \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right) \]  

(28A)

Using Eq. (13A), Eqs. (27A) and (28A) can be rewritten as

\[
\frac{d\psi_s}{d\theta} = \left( \frac{3}{R^0} \right) \psi_s^{2/3} \left[ k_p^0 \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right)^{-1} \left\{ p - p_c^0 - \frac{1}{T_r} \right\} + \left( \frac{\psi_s - \phi_m}{(1 - \phi_m)} \right) p \right] + k_a \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right) \]  

(29A)

\[
\frac{dp}{d\theta} = \left( \frac{3}{R^0} \right) \psi_s^{2/3} \left\{ p - p_c^0 - \frac{1}{T_r} \right\} \left[ 1 - \left( \frac{\psi_s - \phi_m}{(1 - \phi_m)} \right) p \right] + \left[ k_p^0 \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right)^{-1} \right] \right] \]  

(30A)

Eqs. (29A) and (30A) need to be solved simultaneously in order to obtain \(\psi_s\) and \(p\) as functions of time. The initial conditions are: at \(\theta = 0\), \(\psi_s = 1\) and \(p = 1\). At time \(\theta = 0\), Eqs. (29A) and (30A) reduce to

\[
\frac{d\psi_s}{d\theta}_{\theta=0} = \left( \frac{3}{R^0} \right) k_p^0 \left( 1 - p_c^0 \right) + k_a - k_i \]  

(31A)

and

\[
\frac{dp}{d\theta}_{\theta=0} = \left( \frac{3}{R^0} \right) \left( k_p^0 + k_a \right) \left( \frac{1 - p_c^0}{1 - \phi_m} \right) \]  

(32A)

Thus the initial slopes of the plots of the plots of \(\psi_s\) and \(p\) vs. \(\theta\) allows us to compute two of the three coefficients, \(k_s, k_c\) and \(k_p^0\).

At steady state, Eqs. (29A) and (30A) reduce to:

\[
\left[ k_p \left( \psi_s^{\infty} - p_c^0 - \frac{1}{T_r} \left[ 1 - \left( \frac{\psi_s^{\infty} - \phi_m}{(1 - \phi_m)} \right) \right] p^{\infty} \right) \right] + \left[ k_a \left( \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (1 - \phi_m)^{1/3}} \right) - k_i \right] = 0 \]  

(33A)
\[ p^\infty - p^0 = \frac{1}{T} \left[ 1 - \frac{\left( \frac{\psi_s - \phi_m}{1 - \phi_m} \right)}{p^\infty} \right] \]  

(34A)

Substituting \( p^\infty - p^0 \) from Eq. (34A) into Eq. (33A), we obtain

\[ \frac{k_a}{k_r} = \left[ 1 - \frac{1}{\left( \frac{\psi_s^{\infty} - \phi_m}{\psi_s^{\infty} - \phi_m} \right)^{1/3}} \right] \]  

(35A)

From Eqs. (31A), (32A) and (35A), we can obtain the values of all three coefficients. Eqs. (29A) and (30A) can then be solved numerically to obtain \( \psi_s \) and \( p \) as functions of time.

The above equations assume a simpler form for O/W/O double emulsion system, in which water as the internal phase is emulsified in the organic membrane phase which, again, is dispersed in the external water phase. Hence it is called water/membrane/water system. Here, swelling occurs only by occlusion. Since there is no nitric acid in the internal phase, there is no osmotic gradient across the organic membrane.

Hence Eq. (30A) is not required. Moreover, the first term associated with the osmotic coefficient \( k^0 \) in Eq. (29A) can be ignored and hence the reduced form of the equation is

\[ \frac{d\psi_s}{d\theta} = \left( \frac{3}{R^0} \right) \psi_s^{2/3} \left\{ k_a \left[ \frac{\psi_s^{1/3} - (\psi_s - \phi_m)^{1/3}}{1 - (\psi_s - \phi_m)^{1/3}} \right] \right\} \]  

(36A)

At time \( \theta = 0 \), Eq. (36A) reduces to

\[ \frac{d\psi_s}{dt} \bigg|_{\theta=0} = \left( \frac{3}{R^0} \right) (k_a - k_i) \]  

(37A)

Thus the initial slope gives the difference \( k_a - k_i \). Also at steady state, Eq. (36A) reduces to Eq. (35A). The two equations (35A) and (37A) could, in principle, be used to estimate the occlusion and the leakage coefficients.