Modeling and simulation of nanocapsule formation

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Abstract

In this work, a model of spherical nanocapsule formation is developed to describe the solvent diffusion induced phase separation process from an initial homogeneous polymer/ solvent/ nonsolvent system.

The model is based on multicomponent mass transfer phenomena and takes into account the moving boundary induced by solvent extraction of the nanocapsule.

In this model we use the extended version of the Maxwell-Stefan model for diffusion which takes into account of different sized molecules. In effect, polymer/ solvent/ nonsolvent system presents molecules with different molar volumes. Therefore to take into account of the volume occupied by molecules, Fornasiero and al. have extended the Maxwell Stephan formulation for Starkly Different-Sized molecules, assuming that the collision between molecules occurs only if they are of equivalent volume. Therefore the natural state variables are volume fractions. The diffusion coefficient of polymer depends on its concentration.

The developed model is applied to describe nanocapsule formation and to predict the morphology associated with the formation of the thin polymer film. This model is solved numerically using a finite volume method based on the variable grid.

Keywords: Nanocapsule ; Multicomponent diffusion; Phase separation ; Polymer; Modeling

Introduction

Nanocapsule formation is due to the solvent diffusion induced phase separation. In this process, phase separation caused by the diffusion of solvent out of and nonsolvent into the nascent membrane

This process is similar to phase inversion process which is widely used in the fabrication of polymeric membranes for a variety of applications.

In phase inversion processes an initially homogeneous polymer solution becomes thermodynamically unstable due to external effects, and phase separates into a continuous polymer-rich phase that surrounds dispersed polymer-lean droplets. Any one or combination of the following driving forces can induce phase inversion of polymer solutions: temperature (thermal-induced phase separation) [1–3], nonsolvent (nonsolvent-induced phase separation/wet-casting) [4], evaporation (dry-casting) [5–11] and dry wet casting [12,13], water vapor (nonsolvent vapor-induced phase separation) [14–18], reaction [19] and shear stress (shear-induced phase separation) [20]. Many of the above-mentioned studies have included extensive modeling of the mass transfer and phase separation kinetics aimed at prediction and control of the morphology of the final membrane structure [21].

The aim of the present study was to present a model of phases separation coupled with mass transfer for an open system with a moving boundary. The process chosen for modeling is the nanocapsule's formation by emulsion diffusion method.

Nanocapsules formation

Nanocapsules

Nanocapsules are synthetic colloidal systems ranging in size from 10 to 500nm, consisted of a core in which an active ingredient can built-in, and surrounded by a thin membrane of polymer (Fig 1)

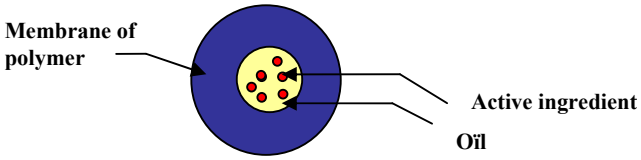

Fig 1 nanocapsule formation

Materials and method

Materials

The polymer used for the nanocapsules formation is poly-ε-caprolactone PCL (Sigma Aldrich Chemica Company Inc., USA). Its average molecular weight (Mw) was given by the supplier as close to 80,000 D. The oil was labrafac lipophilic WL 1349, a mixture of triglycerides of fatty acids caprylic (C8)/capric (C10) from gattefossé. The solvent is the pure ethyl acetate from Laurylab. The stabilizer is polyvinyl alcohol (Mowiols 40-88, 88% hydrolyzed, Mwca 127,000 D from Aldrich Chemical Company). Distilled water saturated with solvent is used as a non-solvent and distilled water as a diluent for the emulsion.

Method

The method proposed to prepare nanocapsules in this study is the emulsification–diffusion. The original of this technique is due to Quintanar-Guerrero [22]; this process involves the emulsification of a partially water-miscible solvent (previously saturated with water), containing the polymer and oil, in an aqueous phase (previously saturated with the solvent), containing a stabilizer. This emulsion is stable. The subsequent addition of large volume of water to the system causes the solvent to diffuse into the external phase, causing the polymer's deposition around the droplets, then the formation of nanocapsules.

Process description

The nanocapsule formation is controlled by two phenomena: the phase separation and the mass transfer and, thus by the competing kinetics between those two phenomena. At the beginning the original system is in a state of thermodynamic equilibrium. The dilution destabilizes this equilibrium. It causes the solvent to diffuse to the external phase and shifts the mixture composition inside the droplets. Thus we have the phase separation inside the droplets and the formation of the distinct nano-phases (polymer-rich phase, solvent rich phase and oil rich- phase) (Fig 2). At the same time the solvent concentration inside the droplet decreases because of the diffusion and the size of nanocapsule decreases.

Eventually, if the composition and the operational conditions are selected accurately, nanocapsules are formed; their formation is principally controlled by the choice oh the initial composition of the system (polymer-oil proportion and polymer oil-solubility) and also by the competition between the formation of oil phase on one hand and the solidification of the polymer rich phase on the other. If the kinetic of the solidification is too fast, the phase rich in polymer becomes too viscous before the domain of oil phase have had enough time to form a continuous core and the oil droplets are fixed inside the polymer matrix, in this case nanospheres are formed.

On the other hand, if the kinetic of solidification of polymer rich phase is too slow the latter does not have a sufficient mechanical stability to withstand the mechanical stresses due to the coalescence of oil nanophases. Consequently the nanocapsules with the polymeric membrane are formed.

Finally, any changes inside the droplet are caused by solvent diffusion to the dilution phase.

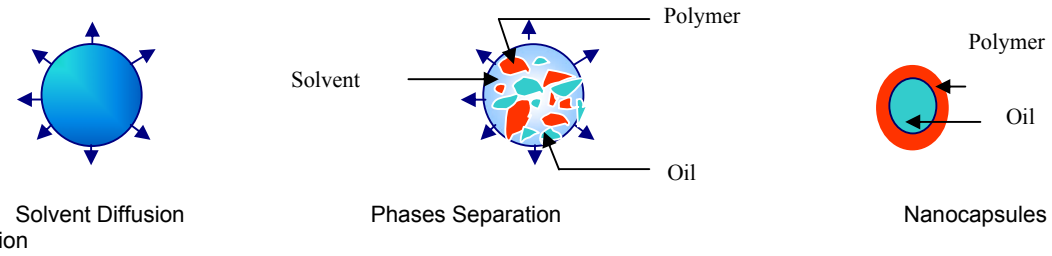

Fig 2: Phase separation during mass transfer processes

So the proposed model must describe a multicomponent mass transfer phenomena coupled with phase separation and must takes into account the moving boundary induced by solvent extraction of the nanocapsule.

Modelling of nanocapsule formation

To model this process we investigate the problem of a single droplet. This droplet is suddenly plunged into infinite aqueous phase. We also assume that outside the droplet the solvent concentration is kept equal to zero because of the perfect stirring and infinite dilution. We represent this system simply as two concentric spheres (Fig 3). The big one represents the aqueous phase and the small one represents the droplet

In the other hand we suppose that the driving force for the mass transfer outside the droplet is proportional to the droplet dissolution rate and we make the following assumptions:

- There are two systems, the external one which represents the exterior of the nanocapsule {solvent + non-solvent} and the internal one {solvent-water + polymer + oil}
- Only three components are inside the nanocapsule (solvent, polymer, oil). The solvent saturated with water has the same behaviour that the solvent alone.
- Nanocapsules are represented by symmetrical spheres
- Diffusion according to r (radius)
- The energy of the mixture inside the nanocapsules is described by the Flory-Huggins thermodynamic model
- we have a moving boundary
- The mass transfer at the interface of the droplet is described by the model of film

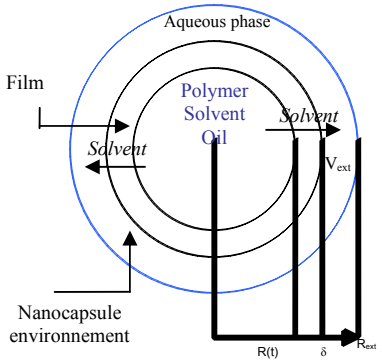

Fig 3: Schematic description of nanocapsule formation

Model formulation for multicomponent system: Theory

In several work, the Maxwell–Stefan approach has been adopted to model the multicomponent mass transfer [23]. In this model the driving forces are given as a linear combination of the material fluxes **(**EQ.1).

$$-c_i \nabla_{T,P} \mu_i = RT \sum_{\substack{j=1 \\ j \neq i}}^{Nc} k_{ij} \left(\frac{N_i}{c_i} - \frac{N_j}{c_j} \right), \qquad i = 1,2,...,Nc \qquad \textbf{Equation 1}$$

where i is one of the diffusing species in the mixture (for polymer/solvent/nonsolvent system subscripts 1, 2 and 3 refer to solvent, nonsolvent and polymer, respectively); c_i is the molar concentration of the component i; c_t is the total molar concentration; $Đ_{ij}$ is the binary Maxwell-Stefan diffusivity; μ_i is the chemical potential, R the ideal gas constant, T the average temperature, N_i is the molar flux of the component i; Nc the number of component, k_{ij} is a friction factor; it's proportional to the product of the molar concentrations:

$$k_{ij} = RT \frac{c_i c_j}{c_T Đ_{ij}} \qquad \textbf{Equation 2}$$

Stefan-Maxwell model has been successfully applied to describe multicomponent diffusion in simple fluid mixtures [23]. Recently, it has also been used to describe transport through polymeric membranes in a solution-diffusion framework. However application of Stefan Maxwell model to a solvent-membrane system presents a great problem: the molar concentration of the membrane is ill-defined because the molecular weight of a membrane is unknown [24].

To circumvent this deficiency, several suggestions have been made [25-30]. Nevertheless the extended Maxwell-Stefan Theory (EMS) developed by Fornasiero and al. remains the more attracting one. This model is developed for solutions of molecules that are starkly different in size.

In the extended Maxwell-Stefan Theory, the polymer molecule is modeled as a collection of connected segments. Each segment has roughly the size of a solvent molecule and all segments in the polymer molecule have identical frictional properties. Compared to

Maxwell-Stefan model, in the EMS the friction factor between the colliding molecules is related to the molar segment concentration rather then the molar species concentration. Fornasiero and al. (EQ.2)

$$k_{ij} = RT\frac{c_i^0 c_j^0}{c_T^0 Đ^0{}_{ij}} \qquad \textbf{Equation 3}$$

Where c_i^0 and c_j^0 are the segment molar concentrations of species *i* and *j*, c_T^0 is the total segment concentration, and $Đ^0{}_{ij}$ is the EMS diffusivity. Then EQ.1 becomes

$$-c_i \nabla_{T,P}\mu_i = RT\sum_{\substack{j=1 \\ j\neq i}}^{Nc}\frac{c_i^0 c_j^0}{c_T^0 Đ^0{}_{ij}}\left(\frac{N_i^0}{c_i^0} - \frac{N_j^0}{c_j^0}\right), \qquad i = 1,2,...,Nc \qquad \textbf{Equation 4}$$

Where the superscript 0 refers to segments, *ns* is the number of segments per molecule of species *i* and N_i^0 is the segment molar flux of the component *i*.

EQ.4 is best rewritten in terms of measurable macroscopic quantities. Fornasiero and al assume that there is no volume change upon mixing and convert the segment mole fraction into a species volume fraction ϕ_i^0 according to

$$c_i^0 = \frac{\phi_i^0}{v_i^0} \qquad \textbf{Equation 5}$$

with $\phi_i^0 = \phi_i$ and $c_i^0 = c_i n_{is}$

n_{is} is the number of segments per molecule. v_i^0 is the molar volume of an *i*-segment. Although choice of the segment unit (and therefore v_i^0) is arbitrary, it is reasonable, based on physical arguments, to assume equal size for all segments, independent of species *i*. With the assumption $v_i^0 = v$ for any species *i*, it can be shown that $c_T^0 = 1/v$. EQ. 4 becomes

$$-c_i \nabla_{T,P}\mu_i = RT\sum_{\substack{j=1 \\ j\neq i}}^{Nc}\frac{1}{Đ^0{}_{ij}}(\phi_i N^0{}_j - \phi_j N^0{}_i), i = 1,2,...,Nc \qquad \textbf{Equation 6}$$

The constraints that must be satisfied are

$$\sum_{i=1}^{Nc}\phi_i = 1$$

$$\sum_{i=1}^{Nc} N^0{}_i = N_t^0 \qquad \textbf{Equation7}$$

Where N_t^0 is the total segment molar flux of a system.

A convenient choice for *v* is the molar volume of the pure solvent or that of the component that has the smallest molecules. This choice of *v* is identical to the choice of the

lattice size in Flory-Huggins polymer solution theory [31] that is widely used to express the chemical potential of a species in a polymer solution or in a membrane as a function of the condensed-phase composition [32].

EMS is consistent with restrictions given by the Gibbs-Duhem equation and by Onsager's reciprocity relations.

Model formulation for multicomponent system: Application to the nanocapsule

Internal problem: inside the nanocapsule

EQ.6 with constraints EQ.7 applies to the inside of the capsule

In this example $i = 1 \;\; or \;\; i = 2 \;\; or \;\; i = 3$

where subscripts 1, 2 and 3 refer to solvent, nonsolvent and polymer, respectively.

Because of the Gibbs-Duhem relationship (Equation 7) only (*Nc* - 1) of the chemical potential gradients are independent

$$\sum_{i=1}^{Nc} n_i \Delta\mu_i = \sum_{i=1}^{Nc} \frac{\phi_i}{n_s v_i^0} \Delta\mu_i = 0$$ **Equation**

where the chemical potentials of each component are given by

$$\frac{\mu_i}{v_i^m} = g + (1-\phi_i)\left(\frac{\partial g}{\partial \phi_i}\right)_{T,P,\phi_{j\neq i}} - \sum_{j=1, j\neq i}^{Nc-1} \phi_j \left(\frac{\partial g}{\partial \phi_j}\right)_{T,P,\phi_{j\neq \phi_i}}$$ **Equation 8**

with $v_i^m = n_s^i v_i^0$, v_i^m is the molar volume of the component *i,* g is the free energy of mixing, given by Flory–Huggins model:

$$g = \sum_{i=1}^{Nc} \frac{\phi_i}{n_s^i v_i^0} \ln\phi_i + \sum_{i=1, i\neq j}^{Nc} \chi_{ij} \frac{\phi_i \phi_j}{n_s^i v_i^0}$$ **Equation 9**

χ_{ij} is the Flory–Huggins interaction parameter between species i and j

Note that the Gibbs free energy is appropriate to systems that approach equilibrium at prescribed temperature and pressure. The physics literature generally prefers the Hemholtz free energy since statistical mechanical studies usually prescribe temperature and volume. Also, they tend to use a per molecule rather than per mole basis, so that the free energies are scaled with *kT* (*k* is the Boltzmann factor) rather than *RT*. These differences have no substantial effect on what follows [33].

In the other hand, the continuity equation for a component *i* in the nanocapsule is obtained from a differential material balance

$$\frac{\partial C_i(t,r)}{\partial t} = -\frac{1}{r^2}\frac{\partial\left(r^2 N_i\right)}{\partial r}$$ **Equation 10**

Therefore we have with segment volume fraction

$$\frac{\partial \phi_i(t,r)}{\partial t} = -\frac{v_i^0}{r^2}\frac{\partial\left(r^2 N^0{}_i\right)}{\partial r} \qquad \textbf{Equation 11}$$

External problem: Outside of the nanocapsule

The mass transfer at the interface of the sphere is described by the model of film. In this model we suppose that all of the resistance to mass transfer is concentrated in a thin film, or layer, adjacent to the phase boundary [23].

So the diffusion process is fully determined by

$$\frac{dn_i}{dt} = K_i\left(C_i^* - C_i\right)S \qquad \textbf{Equation 12}$$

where

n_i : Molar number of the component i (mol)
C_i^* : Equilibrium molar concentration of the component i (mol/m^3)
C_i : Molar concentration of the component i (mol/m^3)
S : The total interfacial area for mass transfer (m^2)
K_i : Mass transfer coefficient (mol/s)

Outside of the nanocapsule, only the solvent diffuses; the flows of other components are assumed to be equal to zero. Accordingly the rate of change of the solvent number of mol is

$$\frac{dn_1}{dt} = K_1\left(C_1^* - C_1\right)S \qquad \textbf{Equation 13}$$

In the other hand we have

$$\frac{dn_1}{dt} = \frac{dC_1 V_{ext}}{dt} = V_{ext}\frac{dC_1}{dt} + C_1\frac{dV_{ext}}{dt} \qquad \textbf{Equation 14}$$

with V_{ext} is the volume of the external phase. It is written as follows

$$V_{ext} = \frac{4\pi}{3}(R_{ext}^3 - R_t^{\,3}) \qquad \textbf{Equation 15}$$

where R_{ext} is the radius of a sphere which represents the nanocapsule's environment and R_t is the nanocapsule radius.

We assume that the nanocapsule radius moves with the velocity dR_t/dt . So the derivative of the volume with respect to the time is written as

$$\frac{dV_{ext}}{dt} = 4\pi(-R_t^{\,2})\frac{dR_t}{dt}$$ **Equation 16**

Upon replacing dV_{ext}/dt and V_{ext} by their values in EQ.15 and rearranging this equation one finds the rate of change of the solvent concentration in the external phase

$$\frac{dC_1}{dt} - \frac{3C_1R_t^{\,2}}{(R_{ext}^3 - R_t^{\,3})}(\frac{dR_t}{dt} - K_1) - \frac{3K_1C_1^*R_t^{\,2}}{(R_{ext}^3 - R_t^{\,3})} = 0$$ **Equation 17**

The rate change of the nanocapsule radius

The objective of this paragraph is to elucidate the correlation mechanism between the nanocapsule radius motion and the mass transfer rate at the interface.

Because of the solvent diffusion toward the external phase, the nanocapsule radius moves with the velocity dR_t/dt . At the interface of the nanocapsule only the solvent diffuses. Accordingly the rate change of the system number of mole corresponds to the solvent flow which it diffused towards the external phase.

The rate change of the system number of mole can be calculated form the following equation

$$\frac{dn_t}{dt} = N_{t(r=R(t))}S$$ **Equation 18**

Where n_t is the total number of moles and $N_{t(r=R(t))}$ is the total molar flux at the interface of the nanocapsule ($r = R_t$) and S is the total interfacial area for mass transfer.

We assume that the molar flux of the polymer and the oil is equal to zero at the interface of the nanocapsule hence

$$N_{2(r=R(t))} = N_{3(r=R(t))} = 0$$ **Equation 19**

Thus $N_{t(r=R(t))} = N_1$ and $\frac{dn_t}{dt} = N_{1(r=R(t))}S$ **Equation 20**

The number of moles of each component is calculated as

$$n_i = \frac{V_i}{v_i^m} = \frac{\phi_i V_t}{n_s v_i^0}$$ **Equation 21**

Using the total number of moles n_t definition one can write

$$n_t = \frac{V_t}{n_s v_i^0}\sum_{i=1}^{Nc}\phi_i$$ **Equation 22**

With this definition the derivative of n_t with respect to time may be written as

$$\frac{dn_t}{dt} = \frac{4\pi R_t^3}{3n_s v_i^0}\sum_{i=1}^{Nc}\frac{d\phi_i}{dt} + \frac{4\pi R_t^2 dR_t}{n_n v_i^0 dt}\sum_{i=1}^{Nc}\phi_i \qquad \textbf{Equation 23}$$

On the other hand at the interface of the nanocapsule, the solvent molar flux inside the nanocapsule is assumed to be equal to the solvent molar flux in the external phase (because of the Flux continuity). Consequently we can write

$$N_1 S = \frac{dn_t}{dt} = K_1\left(C_1^* - C_1\right)S \qquad \textbf{Equation 24}$$

Consequently

$$K_1(C_1^* - C_1)S = \frac{4\pi R_t^3}{3n_s v_i^0}\sum_{i=1}^{Nc}\frac{d\phi_i}{dt} + \frac{4\pi R_t^2 dR_t}{n_n v_i^0 dt}\sum_{i=1}^{Nc}\phi_i \qquad \textbf{Equation 25}$$

The rate change of the nanocapsule radius is written as

$$\frac{R_t}{3n_s v_i^0}\sum_{i=1}^{Nc}\frac{d\phi_i}{dt} + \frac{dR_t}{n_n v_i^0 dt}\sum_{i=1}^{Nc}\phi_i - K_1(C_1^* - C_1) = 0 \qquad \textbf{Equation 26}$$

Boundary conditions

This model will be solved subject to following boundary conditions

At $r = 0 \qquad N_i^0 = 0 \quad i = 1,2,3$ **Equation 27**

At the interfaces the continuities of flux are imposed.

At $r = R_t \qquad N_i^0 = 0 \quad i = 2,3$ **Equation 28**

$$N_t^0 = N_1^0 = K_1(C_1^* - C_1)$$

The equilibrium molar concentration of solvent C_1^* is equal to the molar concentration of solvent at the interface.

$$C_1^* = C_{1(r=R(t)} \qquad \textbf{Equation 29}$$

And it can be writing in term of volume fraction

$$C_1^* = \frac{\phi_{1(r=R(t))}}{n_s^1 v_1^0} \qquad \textbf{Equation 30}$$

Finally we assume that the diffusion coefficient of polymer depends on its concentration.

Numerical resolution

The above equations have been spatially discretized by using the finite volumes method with a variable grid size in order to get a system of differential algebraic equations of time which will be solved using The Petzold–Gear method (DASPG routine of the IMSL package).

Spatial discretization

The domain is initially discretized using a one-dimensional spherical grid directed positively towards the right. To write the scheme of discretization in J, we will indicate by J+1 and J-1 the node located immediately on its right and its left (Fig 4). The "control volume" is centered in J and has a Δr as a dimension. This volume is bounded by j and j-1.

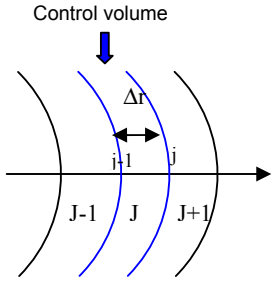

Fig 4: The scheme of discretization

We assume that the flux leaving one control volume is the same as that entering the adjacent volume and inside each volume, both physical and chemical properties are considered constant and equal to the volume-average value.

So by definition $\bar{x}$ the volume-average of the variable x in the volume V is given by the following equation

$$\bar{x} \equiv \frac{1}{V}\int_V x\,dV \qquad \textbf{Equation 31}$$

And for spherical coordinate

$$\bar{x} \equiv \frac{3}{R^3}\int_0^R x r^2\,dr \qquad \textbf{Equation 32}$$

Finally the partials differentials equations are integrated on each of the control volume.

Notice that the boundaries of integration for each volume are variable (because of the moving interface). So we use the Leibniz integral rule to calculate the integral of the continuity equation (EQ.12)

In order to facilitate numerical treatment of the moving interface, the following coordinate transformation is used:

$$\xi = \frac{r}{R(t)} \quad \text{For} \quad 0 \le r \le R(t) \quad \text{and} \quad 0 \le \xi \le 1$$ **Equation 33**

Accordingly

$$\frac{dr}{dt} = \xi \frac{dR(t)}{dt}$$ **Equation 34**

Consequently, the final set of the continuity equation for each component in each volume becomes the following

$$\frac{d}{dt}\int_{r_{j-1}}^{r_j} \frac{4\pi}{3}\phi_i(t,r)r^2 dr = \int_{r_{j-1}}^{r_j} \frac{d\phi_i(t,r)}{dt}4\pi r^2 dr + 4\pi r_{j+1}^2 \phi(t,r_{j+1})\frac{dr_{j+1}}{dt} - 4\pi r_j^2 \phi_i(t,r_j)\frac{dr_j}{dt}$$
$$= -v_i^0 \int_{r_{j-1}}^{r_j} 4\pi \frac{\partial(r^2 N_i^0(r))}{\partial r} dr$$ **Equation 35**

Upon replacing $\frac{dr_j}{dt}$ and $\frac{dr_{j+1}}{dt}$ with their value in EQ.36 and calculation the integral. Eq.36 becomes the following

$$\left.\overline{\frac{\partial\phi(t,\xi)}{\partial t}}\right|_J + \frac{3}{R_t(\xi_j^3 - \xi_{j-1}^3)}((\xi_j^3 \left.\overline{\phi(t,\xi)}\right|_{J+1} - \xi_{j-1}^3 \left.\overline{\phi(t,\xi)}\right|_J)\frac{dR_t}{dt} + v_i^0\left(\xi_j^2\left.\overline{N_i^0}\right|_J - \xi_{j-1}^2\left.\overline{N_i^0}\right|_{J-1}\right)) = 0$$ **Equation 36**

The development of EQ.11 in the case of moving boundaries introduces a new term relative to convection induced by solvent diffusion inside the nanocapsule. This term elucidates the interface motion. It also explains that the solvent diffusion is compensated by the volume reduction.

Indeed during the solvent diffusion the volume of the nanocapsule decrease consequently the total density of the system remains constant.

Simulation

According to the model developed above, a numerical algorithm model has been developed using FORTRAN.

Input/output variables

Input variables and parameters are shown in table.1

Input	Values
Variables	
Initials Composition:	
Solvent volume fraction inside the nanocapsule phi$_{10}$	0.8
Polymer volume Fraction inside the nanocapsule	0.1

phi_{20}	
External solvent concentration (mol/m^3)	
C_{t0}	0
Geometrical parameters	
Radius of droplet (m)	
R_{t0}	2.10^{-6}
Parameters	
Temperature (K)	300
Physical parameters	
Diffusion coefficients (m^2/s)	
D_{12}	10^{-10}
D_{13}	$2\ 10^{-10}$
D_{23}	$(2.10^{-100})^{phi2}$
D_{31}	$(2.10^{-100})^{phi2}$
D_{32}	10^{-10}
Mass transfer coefficient (m/s)	10^{-16}
K_1	5.10^{-10}
Molar volume (m^3/mol)	
v_m	97
Numbers of segments (-)	
ns_1	1
ns_2	714
ns_3	1
Thermodynamical parameters	
Interactions parameters (-)	
χ_{12}	0
χ_{13}	0
χ_{23}	0
Geometrical parameters	
Radius of nanocapsule environment (m)	120.10^{-6}
R_{ext}	1200.10^{-6}

We assume that the diffusion coefficient of polymer solvent (Fig 5) and polymer nonsolvent (Fig 6) are function as polymer volume fraction. So when the polymer solvent fraction increases, these coefficients decrease and tend towards zero. So the molar flux becomes null.

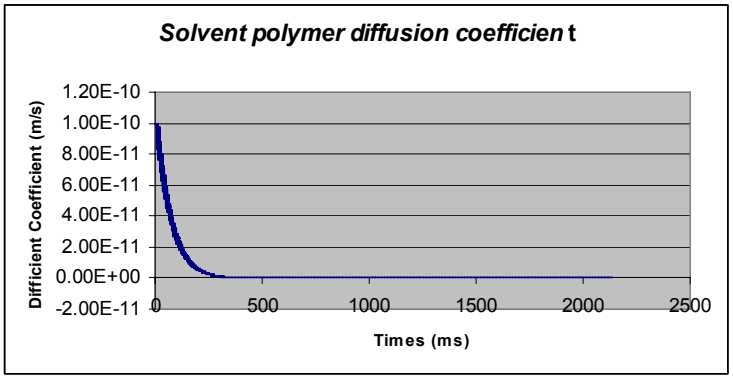

Fig 5 Evolution of polymer solvent diffusion coefficient

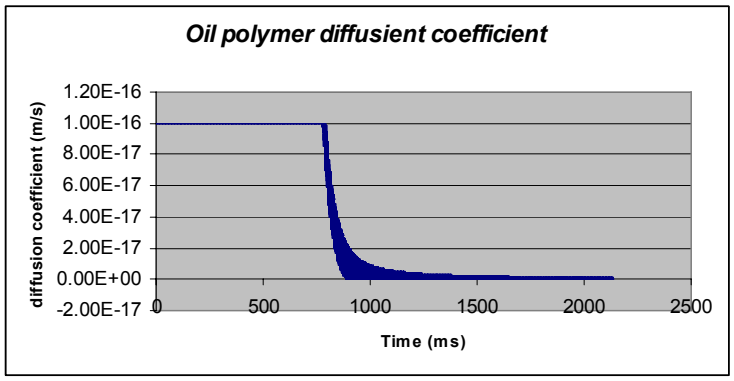

Fig 6 Evolution of polymer nonsolvent diffusion coefficient

In the other hand we suppose that the solvent does not diffuse entirely towards the external phase.

Out put variable

Out put variables are polymer volume fraction, solvent volume fraction, nanocapsule radius and external solvent concentration.

Simulation results

Nanocapsule radius (Fig 7), and external solvent concentration (Fig 8) in response to input composition (table 1) were investigated through simulations.

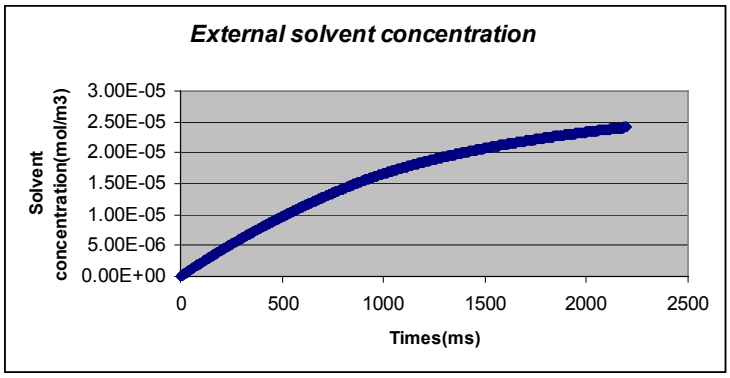

Fig7 Evolution of solvent concentration outside the nanocapsule

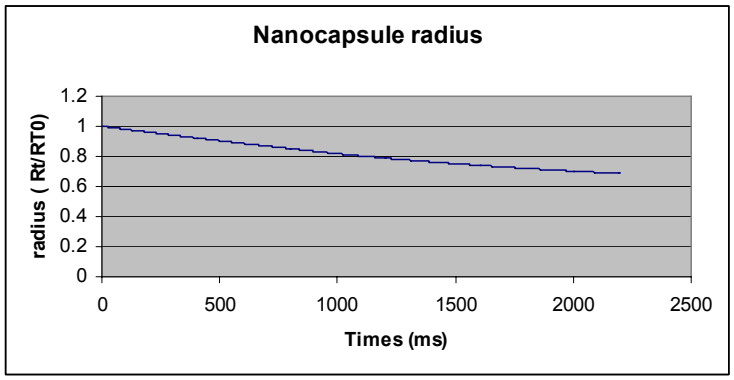

Fig 8 dimensionless radius evolution

The solvent concentration in the external phase increases (Fig 7) and the nanocapsule size decreases (Fig 8). Furthermore polymer and oil volume fraction increase inside the nanocapsule.

In this work we assume that the formation of polymer membrane may be explained exclusively by diffusion phenomena. The diffusion coefficients given in table 1 allow following result which is the increase of the polymer volume fraction at the interface.

The diffusion coefficient of the polymer in the solvent decreases with the increase of the polymer volume fraction (relation given in table 1 and shown in figure 5). When this diffusion coefficient decreases and is nearly null, the polymer diffusion stops. The volume fraction being more important at the interface, we can observe the polymer accumulation.

This phenomenon represents the sudden solidification of the polymer. Consequently the polymer remains at the nanocapsule interface and form a porous membrane around the oil.

To show polymeric membrane formation at the nanocapsule interface, polymer and oil fractions evolution according to space at the beginning and the end of the process are represented on figures from 9 to 12.

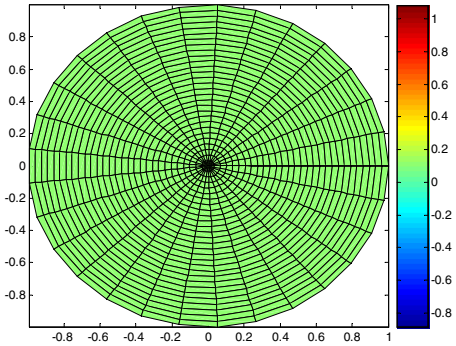

Fig 9 : Oil volume fraction a t=0

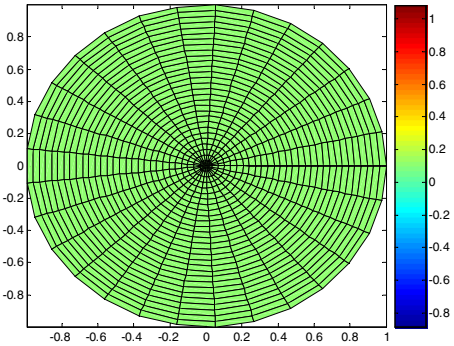

Fig 10 : Polymer volume fraction a t=0

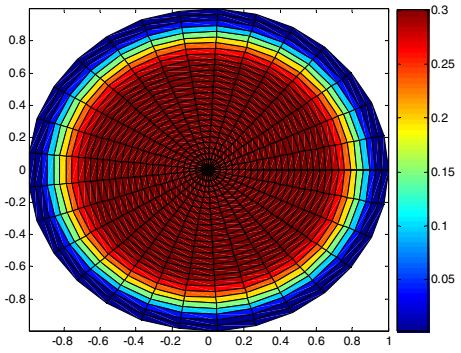

Fig 11: Oil volume fraction at $t=t_{final}$

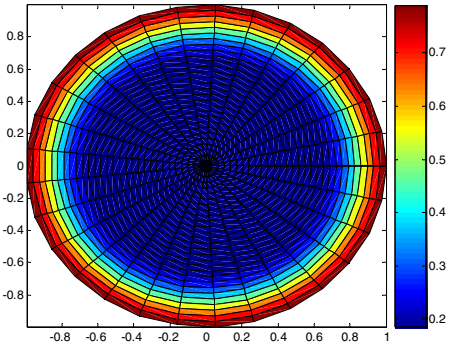

Fig 12: Polymer volume fraction at $t=t_{final}$

As shown in Fig 11 and Fig 12 the polymer volume fraction tends towards 1 at the interface of the nanocapsule and disappears from the center. At the same time the oil becomes more concentrated at the center and disappears from the interface.

Conclusion

A model of nanocapsule formation is developed in this article. This model is able to describe the polymeric membrane formation at the interface of the nanocapsule and takes into account the moving boundary induced by solvent extraction. The diffusion phenomena are described by Maxwell-Stefan equations. In the order to respect the global mass balance, the formalism of Fornasio is adopted and the Maxwell-Stefan equations are rewritten with this formalism. These equations are resolved with the finite volumes method. The phase separation is assumed only by the diffusion coefficients variation with the polymer volume fraction.

The formalism of Fornasio allows the global mass balance conservation with molar volumes between species very different. The diffusion coefficients variation with the polymer volume fraction allows describing the accumulation of the polymer at the interface but these equations are strongly non-linear and stiff. Their resolution is difficult and depends strongly on introduced parameters.

In order to take into account the chemical potential real described by Flory-Huggins in this model with interaction parameters non null, the calculation of phase number to equilibrium and phases composition will be coupled at the resolution of the presented model in this work. So the diffusion coefficients will be constant and the phase separation will be only assumed by the thermodynamic effect.

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