Mecánica Computacional Volumen XV
Compilado por A. Larreteguy y M. Vénere
Bariloche, noviembre de 1995

SURFACE ELASTICITY AND SURFACE VISCOSITY IN A COATING FLOW

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RESUMEN

Se analiza el efecto de los surfactantes adsorbidos sobre el flujo que tiene lugar en la zona de formación de la película del recubridor de ranura. La técnica numérica empleada en este trabajo se basa en el método de elementos finitos y puede manejar adecuadamente los flujos con superficies libres con propiedades interfaciales variables. La completa información producida por el código computacional permite relacionar la dinámica interfacial con los mecanismos involucrados en el transporte de materia: convección y adsorción/desorción. Los resultados presentados muestran que los efectos producidos por la viscosidad y la elasticidad interfacial son semejantes; sin embargo, las condiciones operativas que hacen estos efectos más notables son diferentes.

ABSTRACT

The effect of adsorbed surfactants on the flow that takes place in the film forming zone of the slot coater is examined. The numerical technique employed in this work, that is based on the finite element method, can suitably handle viscous free surfaces with locally varying interfacial properties. The complete information produced by the computational code allows to relate the interfacial dynamics to the mechanism involved in the mass transport process: convection and adsorption/desorption. The results presented show that the effects produced by both interfacial viscosity and interfacial elasticity are rather similar; however, the operating conditions that make them more noticeable are different

INTRODUCTION

Coating operations involve viscous flows in which a thin liquid film is continuously deposited on a moving substrate. These flows, upon which the control and feasibility of a coating process depend, may be considered steady, isothermal and, except for narrow edge regions, two dimensional; also, they are characterized by one or more free surfaces. The uniformity of the film is one of the most important goals of a coating process, a characteristic closely related to the dynamic behavior of the interfaces. Liquids commonly employed in coating operations contain additives, among them surface active agents which are adsorbed at the free surface altering its properties (surface viscosity and surface tension) and this, in turn, may affect the dynamic behavior of the interface.

Despite that surfactants are often used not only in coating technology but also in a great number of practical applications, their influence on the associated flows has not been largely explored. In a previous work, Giavedoni and Saita [1] analyzed the flow occurring in the rear part of the slot coater when the interfacial concentration of surfactant is constant; i.e. they studied a limit case. Also, they presented a technique for introducing the surface viscous terms into the numerical codes employed in the analysis of coating flows. That work is the basis of the present one.

The overall goal of this paper is to numerically study the effects of surface active agents in the flow that takes place at the film forming zone of the slot coater. Figure 1 illustrates the flow domain considered and shows some features of this problem which has been extensively studied by Saito and Scriven [2] when the interface is free of surfactants. This problem is rather complicated; nevertheless, under certain conditions we can attain an approximate solution. The flow in the coating bead is intense; therefore, the mass transport by convection must be much more important than the diffusional process and thus, we may presume that the surfactant concentration is uniform in the liquid phase even near the interface. Then, a concentration jump should exist in the thin interfacial sublayer where the adsorption process takes place and the mass transfer problem is reduced to the free surface where a non-equilibrium concentration of surface-active agents should generally exist. Since the governing equations of this problem are non-linear and strongly coupled because of the interactions between the bulk and the surface phase, the only way of attaining proper results is by means of sophisticated numerical techniques. The one here employed was developed at the University of Minnesota for analyzing free surface flows when the interface is free of surfactants (see e.g. Kistler and Scriven [3]).

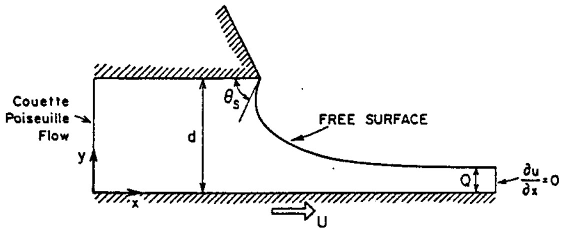

Figure 1: Schematic representation of slot coating flow.

MATHEMATICAL FORMULATION

A. Balance equations for the bulk phase

The flow in the slot coater is steady and isothermic; also, it can be regarded as two-dimensional except for a small region near the edges of the coating device. The liquid is incompressible and Newtonian. The surfactant concentration is presumed uniform in the liquid phase and it remains constant throughout the process of mass transfer from or to the interface. The ambient gas is inviscid and its pressure, which is used as the pressure datum, is arbitrarily set equal to zero. Under these conditions, the mass balance in the bulk phase is described by the continuity equation,

$$\nabla\cdot\mathbf{v}=0. \qquad (1)$$

Since the characteristic dimensions of the coating device are very small, the effect of gravity can be neglected; therefore the balance of momentum results

$$Re\nabla\cdot(\mathbf{v}\,\mathbf{v})-\nabla\cdot\mathbf{T}=\mathbf{0}; \qquad (2)$$

where $\mathbf{T} = -p\mathbf{I}+\left[\nabla\mathbf{v}+(\nabla\mathbf{v})^T\right]$. Equations (1), (2) and the constitutive equation for the Newtonian liquid are written in their dimensionless form. The characteristic scales used are the substrate speed (U) and the clearence between the die and the substrate (d). Pressure and stresses are measured in units of viscous force $(\mu U/d)$, $Re = \rho U d/\mu$ is the Reynolds number, ρ and μ are the density and the viscosity of the liquid phase, respectively.

To complete the mathematical description of the problem we must specify the appropriate boundary conditions; they are as follows

a) On solid surfaces the liquid adheres to the solid; then, on the die wall the components of the velocity vector are

$$u = 0,\ \ v = 0; \quad y = 1,\ \ 0 \le x \le x_S, \qquad (3)$$

and on the moving substrate,

$$u = 1, v = 0; \quad y = 1,\ \ 0 \le x \le x_F \qquad (4)$$

where u and v are the components of the velocity vector in the x and y directions, respectively.

b) Far upstream from the meniscus the flow is 1-D; consequently, the velocity distribution should be parabolic satisfying boundary conditions (3), (4) and also satisfying the net flow rate Q which is measured in units of (Ud). Thus,

$$u = 3(1-2Q)y(y-1) - y + 1,\ v = 0; \quad x = 0,\ 0 \le y \le 1. \qquad (5)$$

c) Far downstream from the slot exit, the flow should be rectilinear; there we impose a zero traction to the normal outflow boundary,

$$\mathbf{T}\cdot\mathbf{n} = \mathbf{0}; \quad x = x_F,\ 0 \le y \le y_{FS}. \qquad (6)$$

The boundary conditions to be imposed along the liquid-air interface are considered in detail in the next section.

B. Interfacial balance equations

In order to obtain an expression for the traction vector at the interface we assume that the following hypotheses hold:

(i) The normal component of the velocity at the interface is zero .

(ii) The total surface mass density is small enough so as to consider the inertial terms negligible.

(iii) There are no surface body forces acting on the interface .

(iv) The interface is Newtonian and the surface stress tensor of the interface with adsorbed surfactants is equal to the stress tensor of the pure interface, the only difference being the coefficients (surface viscosity and surface tension) that in the former case depend on the local concentration of surfactant. Moreover, published experimental results ([4].[5]) show that the total interfacial viscosity is approximately equal to the dilatational surface viscosity (k).

Considering the hypotheses (i)-(v) and the geometry of the interface (i.e., a cylindrical surface), we obtain the folowing dimensionless expression for the traction vector at the free surface:

$$\mathbf{T}\cdot\mathbf{n}=\frac{d}{ds}\left[\left(\frac{\bar{\sigma}(\rho^{(s)})}{Ca}+\bar{\delta}(\rho^{(s)})\frac{dW}{ds}\right)\mathbf{t}\right]. \qquad (7)$$

$\bar{\sigma}(\rho^{(s)})=\sigma/\sigma_M$ and $\bar{\delta}(\rho^{(s)})=\kappa/\mu d$, where $\rho^{(s)}$ is measured in units of the interfacial concentration of surfactants that would exist if the surface were in equilibrium with the adjacent phase (i.e. $\hat{\rho}_o^{(s)}$) In the latter equation s is the dimensionless arc length, W is the interfacial velocity measured in units of U, $\mathbf{t}$ is the unit tangent vector to the free surface pointing in the direction of increasing s and $Ca = \mu U/\sigma$ is the Capillary number defined with the value of $\sigma=\sigma_M$ corresponding to an interface free of surfactants. Also, $\bar{\sigma}(\rho^{(s)})=\sigma/\sigma_M$ and $\bar{\delta}(\rho^{(s)})=\kappa/\mu d$, where $\rho^{(s)}$ is the dimensionless concentration of surfactant at the interface measured in units of the interfacial concentration of surfactants that would exist if the surface were in equilibrium with the adjacent phase (i.e. $\hat{\rho}_o^{(s)}$). It is easy to note that if there are no surfactants at the interface this expression will simplify to the boundary condition usually imposed at a liquid interface.

In order to evaluate Eq. (7) it is necessary to establish a functional relation connecting $\bar{\sigma}(\rho^{(s)})$ and $\bar{\delta}(\rho^{(s)})$ with $\rho^{(s)}$. Additionally, we must write an equation for the interfacial mass balance of solute from which the local surfactant concentration should be evaluated. We make the following assumptions:

(i) There is no chemical reaction at the interface.

(ii) Fick's law is appropriate to describe interfacial diffusion. Data available in the literature ([6],[7]) indicate that surface diffusion coefficients are probably equal to or less than 10^{-6} cm^2/s. Taking into account that the characteristic length of the system is of the order of 10^{-2} cm and that the characteristic velocity is generally greater than 10 cm/s, it is easily verified that the dimensionless number relating the interfacial diffusion to the interfacial convection $\left(D^{(s)}/dU\right)$ is of an order equal to or smaller than 10^{-5} and, therefore, the diffusional transport on the surface will be negligible compared to the convective transport.

(iii) The mass transport between the surface and the bulk is carried out by an adsorption/desorption process of first-order rate. Since the concentration of surfactant in the bulk stays constant even near the free surface, this process is described by: $k_{-1}\hat{\rho}_o^{(s)}(\rho^{(s)}-1)$; where k_{-1} is the kinetic constant.

Considering the foregoing hypotheses, the interfacial mass balance of surfactants reduces to the following dimensionless expression:

$$\frac{d(\rho^{(s)}W)}{ds}=\frac{Ad}{Re}\left(1-\rho^{(s)}\right). \qquad (8)$$

In equation (8), $Ad = k_{-1}d^2\rho/\mu$ is the Adsorption number and $Ad/Re = k_{-1}d/U$ denotes the ratio of adsorption to convective mass transport.

The remaining boundary conditions to be imposed at the interface are independent of the adsorbed surfactants and establish that the free surface is pinned at the separation point $\left(x_S, y_S\right)$ and becomes parallel to the substrate at the outflow plane. Finally, although the surfactant can be adsorbed at the interface, it can not be transferred through it; therefore, the interface is a material surface and the kinematic condition adopts the usual form:

$$\mathbf{v} \cdot \mathbf{n} = 0. \qquad (9)$$

In order to observe how the presence of surfactants affects the coating flow it is necessary to introduce constitutive equations relating the surfactant concentration to the local values of the interfacial tension and the surface viscosity. Tipically, a linear relationship is assumed; thus,

$$\bar{\sigma}\left(\rho^{(s)}\right) = \frac{\sigma}{\sigma_M} = \left(1 - \beta\rho^{(s)}\right), \qquad (10)$$

$$\bar{\delta}\left(\rho^{(s)}\right) = \frac{\kappa\left(\hat{\rho}_o^{(s)}\right)}{\mu d}\rho^{(s)} = \delta\rho^{(s)}, \qquad (11)$$

where $\beta = \left(\sigma_M - \sigma_m\right)/\sigma_M$ is the elastic number, σ_m is the surface tension when $\rho^{(s)} = 1$, $\delta = \kappa\left(\hat{\rho}_o^{(s)}\right)/\mu d$ is the viscosity number and $\kappa\left(\hat{\rho}_o^{(s)}\right)$ is the value of the dilatational surface viscosity at equilibrium.

In the next section we show the more salient features of the numerical technique employed to solve the problem. The way the surface viscosity and surface tension are treated in the dynamic boundary condition and the discretization of the equation representing the mass balance of surfactant are particularly emphasized.

NUMERICAL SOLUTION

The system of equations is discretized using the finite element method for free surface flows developed at the University of Minnesota. This solution technique has been formulated in detail in previous works (see, e.g. Saito and Scriven [2], and Kistler and Scriven [3]), thus we will briefly mention the fundamentals.

Eqs. (8) is weighted with the basis functions used to interpolate the interfacial concentration as well as the free surface location; the weighted residuals are then integrated along the free surface. The following vanishing residuals result

$$R_R^j = \left[\rho^{(s)} W \Phi(s)\right]_{(x_S, y_S)}^{(x_F, y_F)} - \int_{FS}\left[\rho^{(s)} W \frac{d\Phi^j}{ds} + \frac{Ad}{Re}\left(1 - \rho^{(s)}\right)\Phi^j\right] ds, \quad j = 1, 2, \ldots J. \qquad (12)$$

In Eq. (12) the first term on the right hand side is zero when is evaluated at $\left(x_S, y_S\right)$ because $W = 0$ at this point.

In the momentum residuals pertaining to the free surface nodes, the traction vector is replaced by Eq. (10) and the resulting expression is integrated by parts following the procedure suggested by Ruschak [8] for an interface free of surfactants. Thus, we obtain

$$\int_{FS}\Phi^k \mathbf{T} \cdot \mathbf{n} = \left\{\Phi^k(s)\mathbf{t}\left[\frac{1 - \beta\rho^{(s)}}{Ca} + \delta\rho^{(s)}\frac{dW}{ds}\right]\right\}_{(x_S, y_S)}^{(x_F, y_F)} - \int_{FS}\mathbf{t}\frac{d\Phi^k}{ds}\left[\frac{1 - \beta\rho^{(s)}}{Ca} + \delta\rho^{(s)}\frac{dW}{ds}\right] ds. \qquad (13)$$

Since at the separation point the velocity is known (Eq. (3)) we do not need to evaluate Eq. (13) there. Additionally, the boundary conditions imposed to the liquid film at the outflow plane imply **t** = **i** and $\frac{dW}{ds} = 0$ at (x_F, y_F).

The complete set of algebraic equations was simultaneously solved by Newton iteration. Computations were done in a Indy workstation of Silicon Graphics. The convergence criterium adopted was that the norm of the difference between two consecutive approximations should be equal to or smaller than 10^{-6}.

The numerical scheme just described permits to obtain appropriate solutions for a wide range of values of the representative dimensionless parameters of the system (*Re*, *Ca*, *Q*); however, the surfactant distribution presents small oscillations near the separation point when the stagnation point is not present on the free surface. In order to eliminate these oscillations (that never exceeds 2% and that are not associated to oscillations of the interfacial velocity) we implemented two procedures that take into account the convective nature of the mass balance equation. They are as follows

(i) Eq. (8) is integrated along the free surface between $s = 0$ (that is, the separation point) and an arbitrary value of s ; then, the resulting expression is made orthogonal to the trial function $\Phi^k(s)$. Thus we obtain

$$R_R^j = \int_{Fs} \Phi^j \left[\rho^{(s)} W - \frac{Ad}{Re} \int_{s=0}^{s} \left(1 - \rho^{(s)}\right) ds \right] ds = 0, \; j = 1, 2, \ldots, J. \qquad (14)$$

(ii) Eq. (8) is written in finite differences using the first order upwinding scheme proposed by Wassmuth *et al.* [9]. Since the isoparametric transformation maps the actual free surface onto a coordinate line, the following finite difference expression is easily introduced into the finite element code

$$\rho_i^{(s)} = \frac{W^{i+1} - W^i}{s_{i+1} - s_i} + \overline{W} \left\{ \begin{matrix} \dfrac{\rho_{i+1}^{(s)} - \rho_i^{(s)}}{s_{i+1} - s_i} \\ \dfrac{\rho_i^{(s)} - \rho_{i-1}^{(s)}}{s_i - s_{i-1}} \end{matrix} \right\} = \frac{Ad}{Re}\left(1 - \rho_i^{(s)}\right) \qquad (15)$$

In the preceding equation, i is a free surface node in the finite element mesh used to discretize the flow domain; the derivative of ρ is approximated by $\left(\rho_{i+1}^{(s)} - \rho_i^{(s)}\right)/\left(s_{i+1} - s_i\right)$ if $\overline{W} < 0$ and by $\left(\rho_i^{(s)} - \rho_{i-1}^{(s)}\right)/\left(s_i - s_{i-1}\right)$ if $\overline{W} > 0$, where $\overline{W}$ stands for $\frac{1}{2}\left(W^{i+1} + W^i\right)$.

A comparison of the solution obtained with the original scheme (Eq. (12)) and those obtained using Eqs. (14) and (15) is presented in Figure 2 for a sample case. We see that Eq. (18) gives a concentration distribution which still presents oscillations, though smaller than those shown by the curve obtained with Eq. (12); while Eq. (15) produces a result free of oscillations. The integral technique has already proved to be useful to avoid oscillations that may appear in the numerical solution of hyperbolic equations in a completely different problem [10]. The results depicted in Figure 2 also show that the three curves are very similar; this is more significant if we take into account that the differences observed in this variable (concentration of surfactants) are by far the greatest ones we found when comparing the three solutions.

The concentration profiles produced by the integral form of the interfacial mass balance are no longer smooth when a stagnation point appears on the free surface and, somewhere between the

The concentration profiles produced by the integral form of the interfacial mass balance are no longer smooth when a stagnation point appears on the free surface and, somewhere between the separation and the stagnation point, the modulus of the surface velocity is greater than 10^{-2} ; close to the stagnation point the concentration profiles present oscillations whose amplitude rapidly grows when the surface velocity increases. Therefore, we employed Eq. (14) if there was no stagnation point and Eq. (12) otherwise.

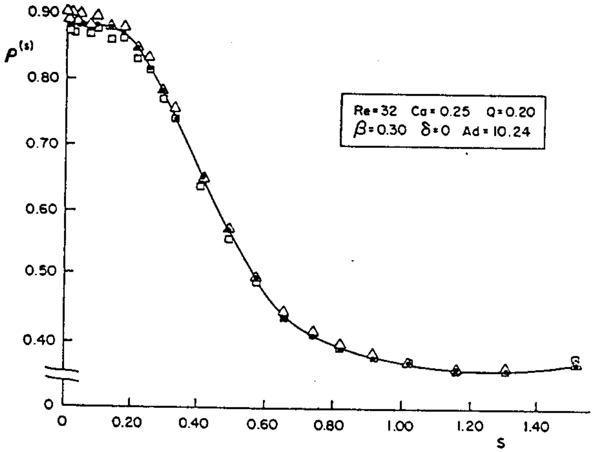

Figure 2 Comparison of the interfacial concentration profiles computed with Eq. (12) Δ, Eq. (14) • and Eq. (15) □. The free surface does not present a stagnation point.

RESULTS

The flow domain was tessellated into 146 elements as it was already mentioned. The non-linear set of algebraic equations has 1396 equations that are simultaneously solved by Newton's method; each Newton iteration takes about 35 seconds in the Indy workstation used to compute the solutions and no more than 5 iterations were needed in order to achieve the convergence criterium adopted. A zero order continuation procedure was used to progressively change any of the parameters of the system.

A. The effect of surface viscosity

Surfactants adsorbed at an interface give rise to surface viscosity which for insoluble films may be as large as 1 surface poise (dyn sec/cm) being usually less than 10^{-2} surface poise for adsorbed films (see e.g., Jaycock and Parfitt [11]). When elastic effects are negligible but the interfacial viscosity is non-zero, the balance of stresses at the free surface depends on the local concentration of surfactant through the constitutive equation relating surface viscosity and $\rho^{(s)}$.

The changes associated with interfacial viscosity are limited to the free surface when δ is small, as it can be observed in Figure 3, where the streamlines calculated by postprocessing the numerical solution are drawn. In fact, the streamlines for $\delta = 0$ and $\delta = 0.25$ are coincident with the exception of the line ending at the stagnation point ($\Psi = 0.20$) and those adjacent to it. If the interfacial viscosity increases, the velocity field of the bulk phase is modified, particularly in the vicinity of the free surface (see inserts): the streamlines corresponding to $\delta = 1$ and $\delta = 1.5$ show that the streamline of 0.20 moves upward and to the interior of the fluid. The recirculation zone is pushed toward the slot entrance and the extension of the 1-D flow region is reduced. (Note that for increasing values of δ the streamline $\Psi = 0.225$ is displaced toward $x = 0$).

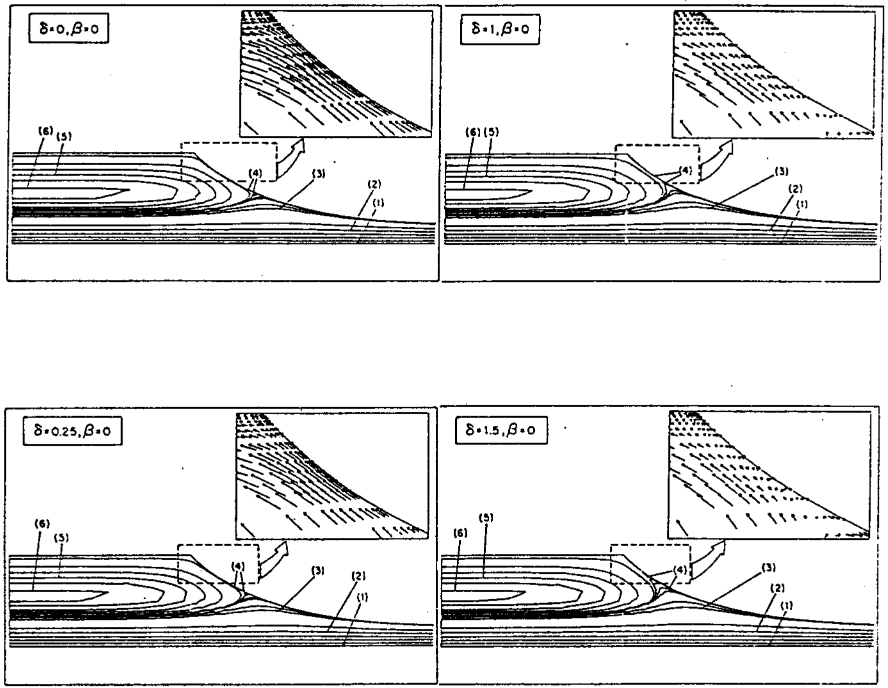

Figure 3: Streamlines for different values of the viscosity number (d); (1) Ψ=0., (2) Ψ=0.12, (3) Ψ=0.19, (4) Ψ=0.20, (5) Ψ=0.215, (6) Ψ=0.225. The inserts show the flow field corresponding to the region enclosed by dashed lines. $Re = 1$, $Ca = 0.05$, $Q = 0.20$ and $Ad = 0.8$.

The results depicted in Figure 3 also show that the free surface shape is not affected by δ, at least in the range of viscosity numbers here considered. According to our numerical calculations, the static contact angle θ_s varies by no more than 1° when δ varies between 0 and 2, either for $Re = 1$ or for $Re = 32$.

B. The effect of surface elasticity

If viscous effects are negligible $(\delta = 0)$ but the interfacial tension varies with the concentration of surfactants, the interface will show elastic effects arising from the surface tension gradients.

Elastic effects affect almost exclusively the interfacial velocity when β is very small, but as the elasticity number increases they influence a greater zone of the bulk phase, as it is illustrated by the streamlines drawn in Figure 4 (the inserts correspond to details of the flow field near the free surface). The displacement of the streamline corresponding to $\Psi = 0.20$ upward and toward the inner mass of fluid, shifts the recirculation zone toward $x = 0$ and therefore, the extension of the 1-D flow region diminishes. If Figs. 4 and 3 are compared it is clear that surface elasticity induces changes in the flow field very similar to those induced by surface viscosity.

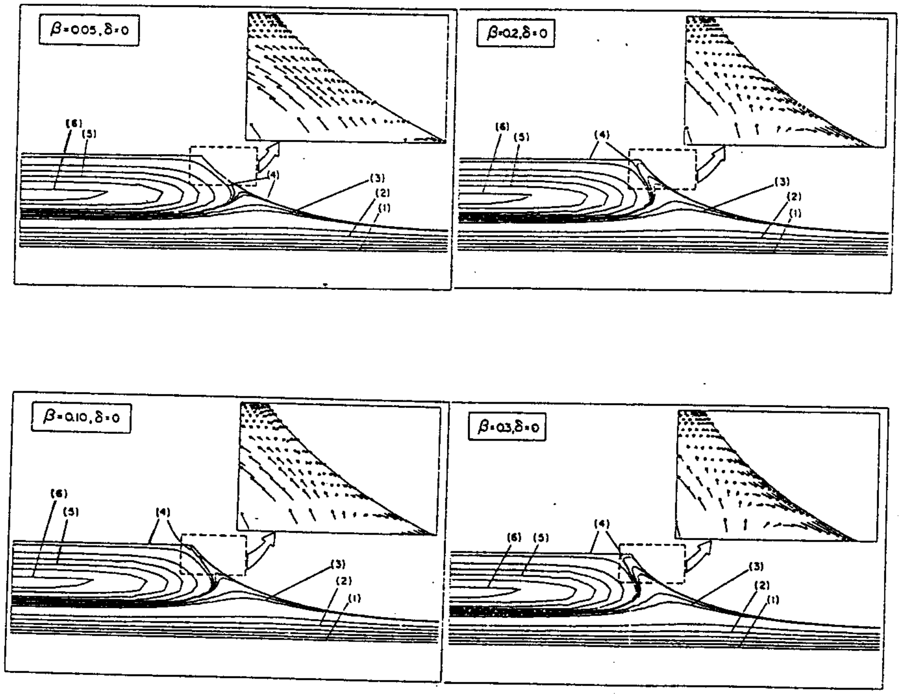

Figure 4: Streamlines for different values of the elasticity number (b); (1) Ψ=0., (2) Ψ=0.12, (3) Ψ=0.19, (4) Ψ=0.20, (5) Ψ=0.215, (6) Ψ=0.225. The inserts show the flow field corresponding to the region enclosed by dashed lines. $Re = 1$, $Ca = 0.05$, $Q = 0.20$ and $Ad = 0.8$.

The inserts in Figure 4 show that the liquid in the vicinity of the free surface moves slowly for small β. In fact, not only at the free surface but also in its vicinity the fluid velocities are considerably smaller for $\beta = 0.05$ than for $\beta = 0$; though the values of $\left(\partial v_s / \partial n\right)_{FS}$ are clearly larger when $\beta = 0.05$. For incipient values of β, W diminishes favouring the action of the sorption process that works to reduce the concentration gradients. When the stagnation point is no longer present ($\beta > 0.067$), any further increase of β produces greater values of the velocity (at the interface and its surroundings) as it can be observed from results corresponding to $\beta \geq 0.1$. Again, the system tends to reduce the velocity gradients responsible for the non-equilibrium state and the boundary conditions at both ends of the interface ($W = 0$, $s = 0$; $W \rightarrow 1$, $s \rightarrow \infty$) preclude that this happens.

CONCLUDING REMARKS

In this work we show that the finite element method combined with a convenient parametrization of the free surface can be easily extended to include the case in which there are surface-active agents adsorbed at the interface. We present three different discrete forms of the interfacial mass balance, one of them is based on a finite difference scheme. Although, these three formulations usually give similar results, in some cases the interfacial concentration presents oscillations depending upon the discrete form employed. Numerical tests indicate that the solutions computed using, either the finite difference approximation or the residuals of the differential mass balance equation, do not oscillate when there is a stagnation point at the interface, whereas, the residuals of the integral form of the mass balance produce better solutions in the opposite situation.

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