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Construction and analysis of some micellization–adsorption models

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Received 10 February 1992

Abstract. This paper presents mathematical models for the micellization and adsorption processes that occur in many surfactants solutions, and which confer the fundamental characteristics of these solutions. The viability of the models is demonstrated by reference to experiment, using both theoretical and numerical analysis, whilst the detailed thermodynamics incorporated in the modelling permits a quantitative investigation of the kinetics of the processes. In particular, the interplay between diffusion and reaction rates, and the implication of this on certain modelling assumptions, is studied, and the effect of various physical parameters, on both kinetic and equilibrium behaviour, quantified. An important aspect of the work is the development of efficient numerical techniques to facilitate the study, and these are outlined in the paper.

1. Introduction

Interfacial properties of surfactant solutions such as soaps, detergents and emulsifying agents are largely determined by the process of micellization and adsorption exhibited by these colloidal systems. It is therefore important to understand the mechanisms by which these processes occur, and to be able to quantify their effects. A model for micellization—the process of agglomeration by which individual surfactant molecules (monomers) combine to form larger molecular groups (micelles)—is presented in section 2. This follows [8] and consists of the so-called Becker–Döring (BD) coagulation–fragmentation equations, together with thermodynamic models for the rate coefficients involved. The model is analysed in section 3, where it is shown to predict many important, experimentally observed, micellization characteristics. In section 4 adsorption processes are considered, and a micellization–adsorption model proposed. This model involves a novel adsorption equation, and analysis of this shows how it may be considered a generalization of the widely used Langmuir isotherm relation. The analysis indicates when this isotherm expression may be considered a valid approximation to the more general equation, and thus provides insight into the underlying physical processes. An efficient numerical scheme for treating the large system of reaction–diffusion equations of the micellization–adsorption model is outlined in section 5 and results presented. Finally, in section 6, the problem of modelling turbulence in conjunction with micellization and adsorption is addressed. A simple extension of the previous model is proposed and some numerical results considered.

2. The stepwise association model: Becker–Döring equations

In many surfactant solutions the dominant mechanism by which micellization occurs

is that of stepwise association-dissociation, and the process may be modelled by the BD equations [6]

$$\begin{aligned} \dot{C}_1 &= -J_2 - \sum_{r=2}^{\infty} J_r \\ \dot{C}_r &= J_r - J_{r+1} \quad r = 2, 3, \dots \end{aligned} \tag{1}$$

where $C_r(t)$ denotes the concentration of micelles containing r monomeric units at time t , and

$$J_r = a_{r-1} C_1 C_{r-1} - b_r C_r \quad r = 2, 3, \dots \tag{2}$$

for suitable rate coefficients a_{r-1}, b_r . These equations have been the subject of much theoretical research [2, 4, 5, 7, 16]. We note here that if $\{C_r\}_{r=1}^{\infty}$ satisfy the BD equations then the total surfactant density $\rho = \sum_{r=1}^{\infty} r C_r$ remains constant (see [5]). We are concerned here with dilute micellar systems. For these, agglomeration is diffusion limited [8] so that we may write $a_r = \alpha$ (constant) $r = 1, 2, \dots$. The b_r may be modelled through the use of chemical potentials. We may write (see [8, 18])

$$b_{r+1} = \alpha \bar{C} \exp\left(\frac{\eta_r - \mu_1^0}{RT}\right) \quad r = 1, 2, \dots \tag{3}$$

where $\bar{C} = \sum_{r=1}^{\infty} \bar{C}_r$ (\bar{C}_r being the equilibrium value of C_r), R is the universal gas constant, T the temperature and $\eta_r = \mu_{r+1}^0 - \mu_r^0$ (μ_r^0 being the standard chemical potential of micelles of size r). The η_r may be modelled (see [3, 8]) for certain positive constants A, B and D :

$$\eta_r \approx A + \frac{2}{3} B r^{1/3} + \frac{4}{3} D r^{1/3} \quad r = 1, 2, \dots \tag{4}$$

This representation for η_r completes the specification of the micellization model (up to the constants A, B and D). The following analysis demonstrates the suitability of this model and, in addition, allows estimates for A, B and D to be computed.

3. Analysis of the micellization model

From consideration of equation (3) it is easy to show that $\bar{C}_{r+1} < \bar{C}_r \Leftrightarrow \eta_r > \bar{\mu}_1$, and from equation (4) the graph of η_r is seen to be of the form shown in figure 1. Thus,

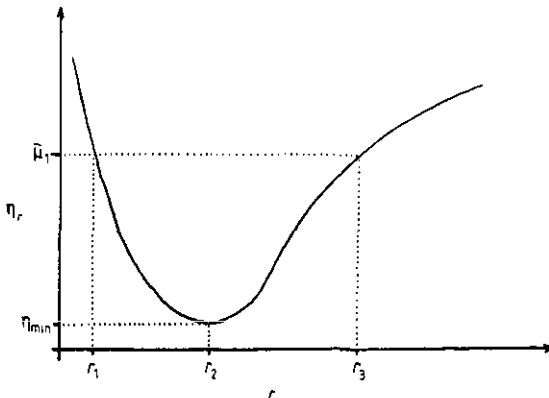


Figure 1. The graph of η_r .

provided $\bar{\mu}_1 > \eta_{\min}$, a distribution of equilibrium concentrations as in figure 2 is obtained. This is known to be constant both with experimental findings [1], and other equilibria thermodynamic treatments [12]. By reference to such results, the coefficients A , B and D may then be fitted. Taking $r_1 = 10$, $r_2 = 50$, $r_3 = 100$ as typical, and with $T = 300$ K, $\mu_1^0 = 10^5$ J mol⁻¹ and $\alpha = 10^{10}$ (mol l⁻¹)⁻¹ s⁻¹, it is easily shown (see [17]) that suitable values for these coefficients are $A = 0.167814 \times 10^5$ J mol⁻¹, $B = 0.142010 \times 10^6$ J mol⁻¹ and $D = 0.523171 \times 10^4$ J mol⁻¹.

The phenomenon of a critical micellization concentration (CMC) is also predicted by the model. Solving a truncated equilibrium system (truncated at $r = N$ ($=200$) by setting $\bar{C}_r = 0$ for $r > N$), and with the parameter values quoted above, the results of figure 3 were obtained. ($N = 200$ is taken since, for most systems, micelles of greater size do not occur in measurable quantities.)

These results fit in well with the concept of a CMC. Further, the predicted temperature dependence of this critical value is as expected for non-ionic surfactants [11]—the onset of agglomeration being repressed by an increase in temperature.

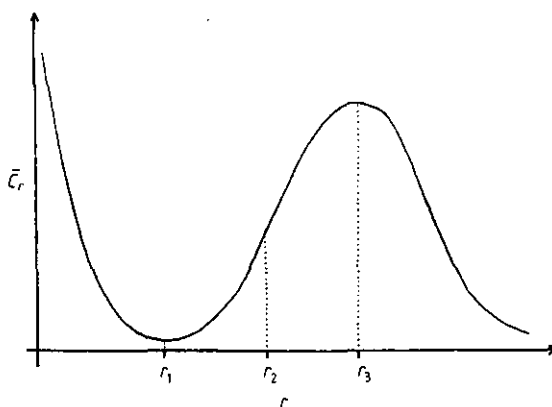


Figure 2. The distribution of \bar{C}_r .

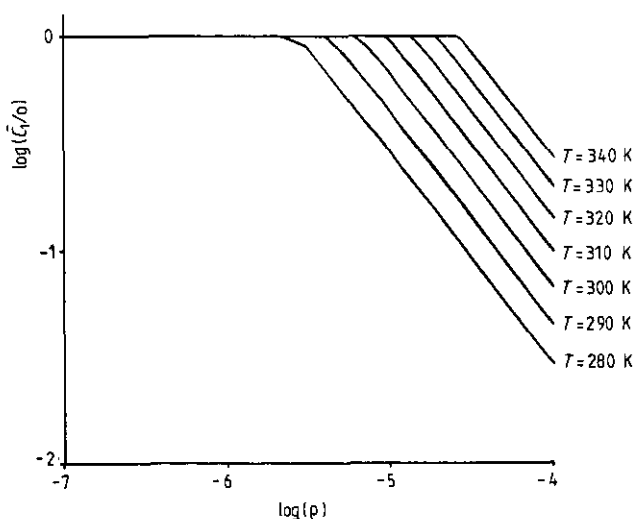


Figure 3. The dependence of \bar{C}_1 on ρ .

Finally, we can simulate the effect of a perturbation experiment by specifying initial concentrations distinct from the equilibria, and then solving, numerically, the dynamical system (1) (truncated at some C_N). A natural choice for an initial concentration distribution is one corresponding to an equilibrium state prior to perturbation. Further, since scaling the forward rate coefficient α does not affect the equilibrium profile, the effects of such a scaling on micellization kinetics may be investigated.

Taking $N = 200$, $T = 310$ K, with an initial distribution obtained as an equilibrium state for $T = 300$ K, and using a simple predictor-corrector numerical scheme the results of figures 4 and 5 were obtained. These not only show the influence of α on re-equilibration kinetics but also the existence of two distinct relaxation times (only relaxation curves for micelles of size 100 are depicted as micelles of other sizes show

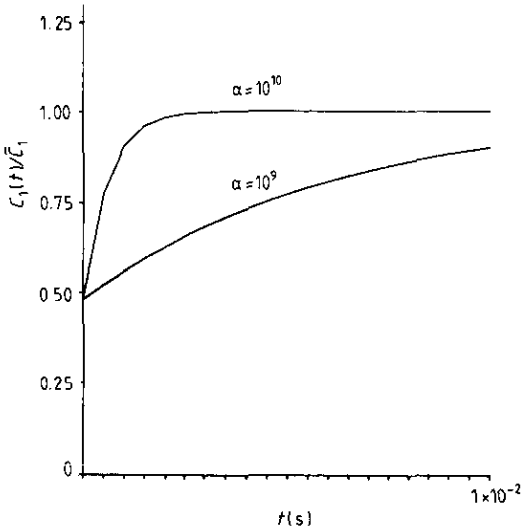


Figure 4. C_1 relaxation kinetics.

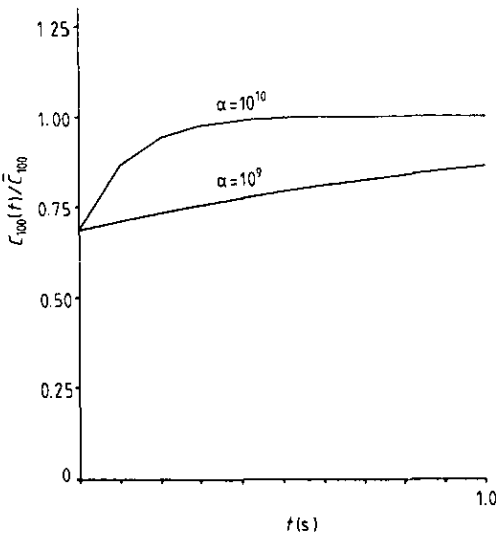


Figure 5. C_{100} relaxation kinetics.

similar response characteristics). This is in quantitative agreement with experimentation [2].

This micellization model is next extended to incorporate the inevitable adsorption processes that occur at interfaces of a surfactant solution. The interaction between the two processes can then be investigated.

4. A micellization-adsorption model

For a micellar system exhibiting no convective flow, a rectangular symmetry and with a plane interface, say at $x = 0$, we have a micellization-adsorption model given by the system of reaction-diffusion equations

$$\frac{\partial}{\partial t} C_r(x, t) = D_r \frac{\partial^2}{\partial x^2} C_r(x, t) + \dot{C}_r(x, t) \quad x > 0 \quad t > 0 \quad r = 1, 2, \dots \tag{5}$$

where D_r denotes the diffusion coefficient for micelles of size r , and $\dot{C}_r(x, t)$ is the rate of change C_r due to micellization as modelled by spatially dependent BD equations (cf equation (1)). Denoting the surface concentration of adsorbed monomer at $x = 0$ by $\Gamma(t)$ then the mass balance boundary conditions for this model are

$$D_1 \frac{\partial}{\partial x} C_1(0, t) = \frac{d}{dt} \Gamma(t) \quad t > 0 \tag{6}$$

$$\frac{\partial}{\partial x} C_r(0, t) = 0 \quad t > 0 \quad r = 2, 3, \dots$$

$$\lim_{x \rightarrow \infty} \left(\frac{\partial}{\partial x} C_r(x, t) \right) = 0 \quad t > 0 \quad r = 1, 2, \dots$$

Suitable initial conditions are

$$C_r(x, 0) = \bar{C}_r \quad x > 0 \quad r = 1, 2, \dots$$

and

$$\Gamma(0) = 0.$$

Here $\{\bar{C}_r\}_{r=1}^\infty$ are the spatially homogeneous equilibrium solutions of the BD equations.

A model for the adsorption process will, typically, be an equation of the form

$$F\left(\Gamma(t), \dot{\Gamma}(t), \Lambda(t), \dot{\Lambda}(t), D_1 \frac{\partial}{\partial x} C_1(0, t)\right) = 0 \quad t > 0 \tag{7}$$

where Λ is the subsurface concentration of monomer. The form of equation (7) used here is that proposed in [14, 15], and is given by

$$\frac{d}{dt} \Gamma(t) = k_1 \Lambda(t) \left(1 - \frac{\Gamma(t)}{\hat{\Gamma}} \right) - k_2 \Gamma(t) \tag{8}$$

where k_1 and k_2 are rate constants for adsorption and desorption, respectively. An important feature of this last equation lies in its connection to the more frequently used Langmuir isotherm adsorption relation [10]

$$\Gamma(t) = \frac{\gamma \hat{\Gamma} \Lambda(t)}{1 + \gamma \Lambda(t)}. \tag{9}$$

Letting $t \rightarrow \infty$ in equation (8) we obtain the equilibrium Langmuir relation

$$\Gamma^\infty = \frac{\gamma \hat{\Gamma} \Lambda^\infty}{1 + \gamma \Lambda^\infty}$$

where $\gamma = k_1/k_2 \hat{\Gamma}$. This suggests that equation (9) is an approximation to equation (8) and, in view of the wide application of the Langmuir isotherm, it is important to know when such an approximation is permissible. By combining equations (8) and (6) and performing some standard non-dimensional and perturbation analysis it can be shown (see [15, 17]) that equation (9) does indeed represent a valid approximation to equation (8), provided

$$\frac{D_1}{\gamma^2 k_2} \ll 1 \quad \frac{k_1}{\lambda k_2} > 1$$

λ being some characteristic length scale. Noting that timescales for adsorption, desorption and diffusion are given by λ/k_1 , $1/k_2$ and λ^2/D_1 , respectively, we see that the above constraints correspond to the requirement that timescales for adsorption and desorption are much smaller than that for diffusion. In most cases of practical interest these conditions do in fact hold and the Langmuir isotherm, equation (9) becomes an acceptable alternative to equation (8).

5. Numerical analysis of the micellization-adsorption model

Attention here is restricted to the use of finite-difference techniques for obtaining numerical solutions of the micellization-adsorption model proposed in the preceding section. As with the simple micellization model of section 2, it is first necessary to truncate the systems of equations involved at some value of N . Since, as previously noted, $N = 200$ represents a realistic value, the size of the resulting systems becomes a significant factor in the choice of numerical scheme; ways to reduce computational time must be considered. Firstly the use of a non-uniform spatial grid is natural since the nature of the adsorption process leads to large concentration gradients close to the adsorbing surface ($x = 0$), which decrease with increasing distance from this surface. A suitable discretization for x is, therefore

$$x_i = x^\infty \left(\frac{i}{M} \right)^p \quad i = 0, 1, \dots, m$$

where $x^\infty > 0$ is sufficiently large to be considered infinitely far from $x = 0$, M is a positive integer defining the number of grid points to be taken, and $p > 1$ provides the transformation from a uniform to a non-uniform grid. Secondly, by approximating the BD reaction terms \dot{C}_r , $r = 1, 2, \dots, N$ using

$$\begin{aligned} \dot{C}_{li}^j &\approx -(\alpha C_{li}^j C_{lj}^{j-1} - b_2 C_{2,i}^{j-1}) - \sum_{s=2}^N (\alpha C_{li}^j C_{s,i}^{j-1} - b_s C_{s,i}^{j-1}) \\ \dot{C}_{r,i}^j &\approx (\alpha C_{li}^j C_{r-1,i}^j - b_r C_{r,i}^j) - (\alpha C_{li}^j C_{r,i}^j - b_{r+1} C_{r+1,i}^{j-1}) \quad r = 2, 3, \dots, N-1 \\ \dot{C}_{N,i}^j &\approx \alpha C_{li}^j C_{N-1,i}^j - b_N C_{N,i}^j \quad i = 1, 2, \dots, M-1 \end{aligned}$$

where $C_{r,i}^j = C_r(x_i, t_j)$, together with standard difference approximations for the t and x derivatives in the reaction-diffusion equations, we obtain N systems of linear equations which, if considered sequentially ($r = 1, r = 2$, etc.) form easily solved tridiagonal systems.

To test this approach we begin by considering a single solute (non-aggregating) system and taking, as an adsorption equation, the linear isotherm relation

$$\Gamma(t) = K\Lambda(t) \quad t > 0$$

K being some isotherm constant. The linearity of the resulting model then permits the analytic solution

$$C_1(x, t) = \bar{C}_1 \left[1 - \exp\left(\frac{Kx + D_1t}{K^2}\right) \operatorname{erfc}\left(\frac{Kx + 2D_1t}{2K\sqrt{D_1t}}\right) \right]$$

so that

$$\Gamma(t) = K\bar{C}_1 \left[1 - \exp\left(\frac{D_1t}{K^2}\right) \operatorname{erfc}\left(\frac{\sqrt{D_1t}}{K}\right) \right],$$

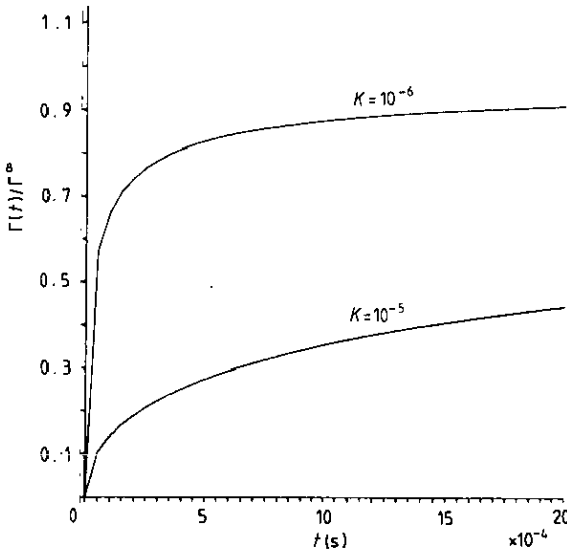


Figure 6. Analytic adsorption curves for $K = 10^{-6}$ and 10^{-5} .

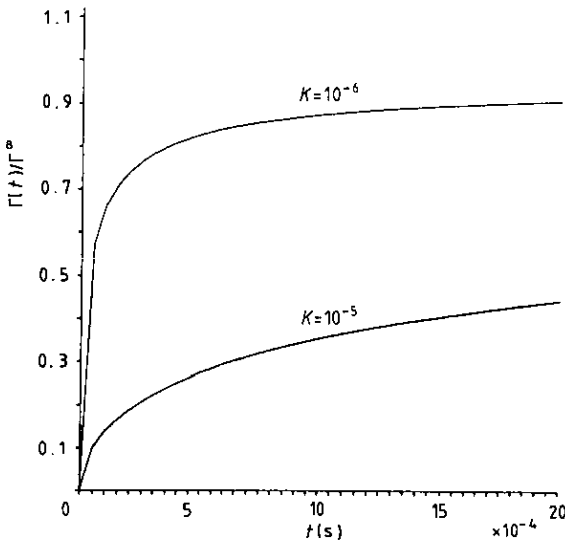


Figure 7. Numeric adsorption curves for $K = 10^{-6}$ and 10^{-5} .

Figure 6 shows two adsorption curves obtained from this solution using different values of the parameter K . Increasing K is seen to decrease the relative adsorption rate. This follows since, from the equilibrium relation $\Gamma^\infty = K\bar{C}_1$, we see that K reflects the adsorptive capacity of the surface for a given \bar{C}_1 . Corresponding numerical results computed using the iterative semi-implicit finite-difference approach outlined above are presented in figure 7. Good agreement with the analytical results is evident.

Applying the scheme to the full micellization-adsorption model, using the Langmuir relation (9) and with $T = 300$ K, $D_1 = 2 \times 10^{-8}$ m² s⁻¹, $D_r = 6 \times 10^{-8}$ m² s⁻¹ ($r > 1$), $\gamma = 10^3$ m³ mol⁻¹ and $\hat{\Gamma} = 10^{-6}$ mol m⁻² (with other parameter values as for the micellization model of sections 2 and 3), the results of figures 8 and 9 were obtained. These show the effects of variations in ρ and α upon adsorption rates. As can be seen, adsorption

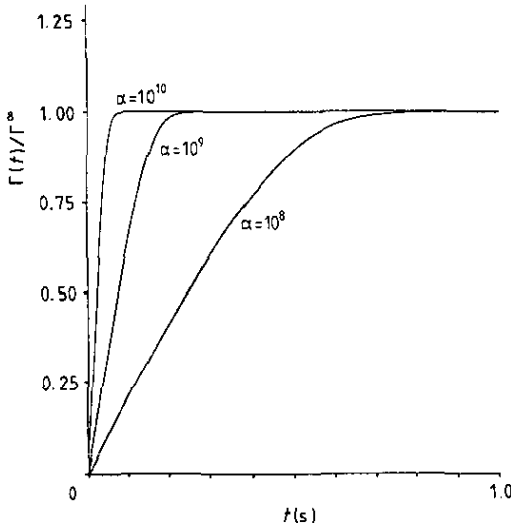


Figure 8. Adsorption rates for $\rho = 10^{-2}$ mol l⁻¹ and different values of α .

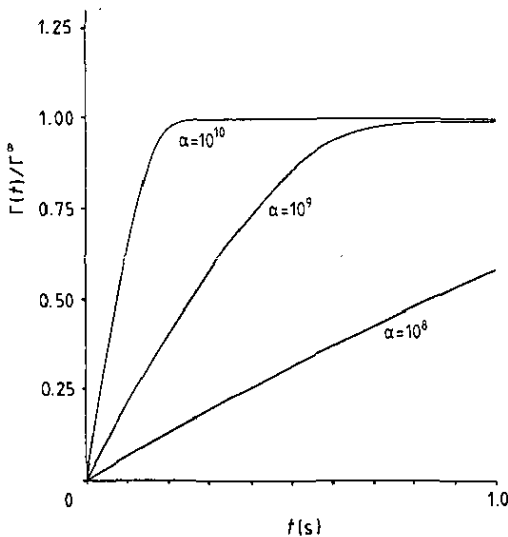


Figure 9. Adsorption rates for $\rho = 10^{-3}$ mol l⁻¹ and different values of α .

rates decrease with both ρ and α . Bearing in mind that the surfactant concentrations used here are well above the CMC (see figure 3) this is, qualitatively, as one might expect.

In reality, of course, most surfactant solutions are likely to exhibit convective transport and, that being the case, we conclude by considering how turbulent convection might be modelled within the foregoing model.

6. Model including turbulent convection

With the addition of convection the general transport equations to be considered would be

$$\frac{\partial}{\partial t} C_r = D_r \nabla^2 C_r + \dot{C}_r - \nabla \cdot (C_r \mathbf{v}) \quad t > 0 \quad r = 1, 2, \dots$$

where \mathbf{v} denotes the fluid velocity.

As we require \mathbf{v} to be descriptive of some form of turbulence, one approach, following [9] (see also [13]), would be to simulate \mathbf{v} statistically from a multivariate normal distribution in such a way that the expected value, $E[\mathbf{v}]$, was zero. The fluid flow would then be ‘statistically stationary’. Further, by adopting a two- or three-dimensional model \mathbf{v} could also be generated in such a way as to guarantee incompressibility, i.e. such that $\nabla \cdot \mathbf{v} = 0$ at each instant [9]. There are, however, several difficulties with (and objections to) this approach in the present context. Firstly, a two- or three-dimensional model would be computationally very expensive to study and, in addition, it is not clear precisely which geometries would be relevant. Secondly, the validity of specifying independent fluid velocities to arbitrarily close points (in space) is questionable. Also, it does not seem sensible to allow fluid velocities close to an interface to be arbitrarily large in magnitude. In view of these remarks we prefer to retain a one-dimensional model, namely

$$\frac{\partial}{\partial t} C_r = D_r \frac{\partial^2}{\partial x^2} C_r + \dot{C}_r - \left(v \frac{\partial}{\partial x} C_r + C_r \frac{\partial}{\partial x} v \right)$$

and to model $v(x, t)$ as

$$v(x, t) = \frac{x}{x^\infty} v^\infty(t) \quad 0 < x < x^\infty$$

where, as before, $x^\infty > 0$ represents a distance to be considered ‘infinitely far’ from the surface, and

$$v^\infty(t) \sim N(0, \sigma^2) \quad \text{for each instant } t.$$

In this way we ensure zero velocity at the interface and the flow becomes both ‘statistically stationary’ and ‘statistically incompressible’.

Numerics for this model are straightforward extensions of those for the previous diffusive transport model and results can then be compared with those already obtained. Output obtained suggests that the addition of this type of turbulence has little, if any effect, upon adsorption rates. Figures 10 and 11 show some typical results. Figure 10 shows the result from a single simulation of the turbulence model and figure 11 the result averaged over 50 such simulations.

The difference between the adsorption curves depicted in figure 11 is, in a sense, a maximum: it is not affected by further increases in the turbulence parameter σ .

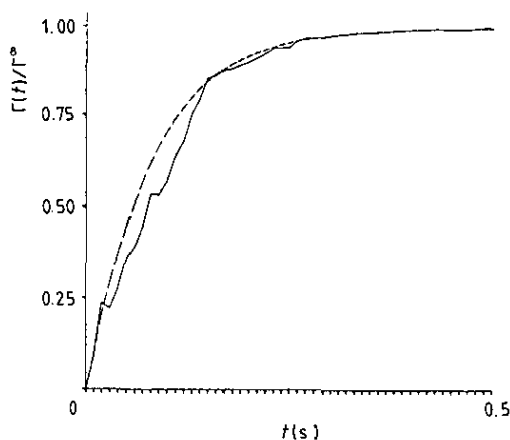


Figure 10. The effect of turbulence on adsorption: result from a single simulation. Full line, adsorption with turbulence; broken line, adsorption with no turbulence.

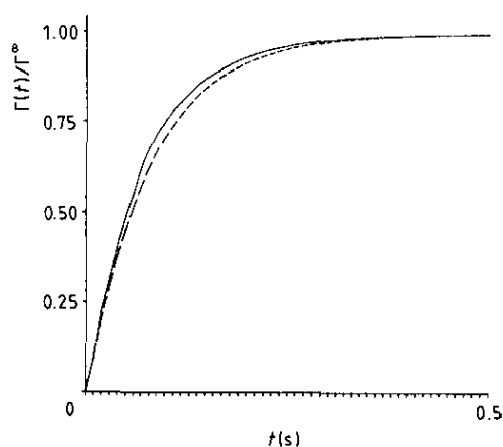


Figure 11. The effect of turbulence on adsorption: result averaged over 50 simulations. Full line, adsorption with turbulence; broken line, adsorption with no turbulence.

7. Conclusions

Models for the micellization and adsorption processes that occur in surfactant solutions have been proposed, and the viability of these demonstrated—theoretically and numerically. The micellization model involves detailed, thermodynamically derived, expressions for the reaction rate coefficients, and this has allowed a quantitative study of the influence of various physical/model parameters on both the kinetic and asymptotic behaviour of the process. In modelling adsorption a non-equilibrium adsorption equation has been proposed and studied. This equation has been shown to constitute a model for the adsorption process that is more general than that provided by the often used Langmuir isotherm. By studying the relation between the two we have derived specific constraints on the use of the Langmuir isotherm as an approximation to the more general equation. An efficient numerical scheme for studying the dynamics of the micellization-adsorption model has been devised and discussed, and results produced from this presented. These indicate the value of the models as a means of studying and quantifying the roles of the various parameters that characterize

colloidal systems. Finally, we have considered one way in which turbulent convective transport might be modelled in the context of micellization-adsorption, and presented results produced by this approach.

Acknowledgments

The authors would like to acknowledge many helpful conversations with Professor Denver Hall, Unilever Research Laboratory, Port Sunlight.

Appendix. Glossary

A, B, D	coefficients in the model for η_r
C_r	concentration of micelles of size r
$C_{r,i}^j$	discretized value $C_r(x_i, t_j)$
\bar{C}_r	equilibrium value of C_r
\dot{C}_r	rate of change of C_r due to micellization
C	total micellar concentration $\sum_{r=1}^{\infty} C_r$
\bar{C}	equilibrium value of C
D_r	diffusion coefficient of micelles of size r
J_r	contribution to \dot{C}_r from association of micelles of size $r-1$ and dissociation of micelles of size r
K	linear isotherm constant
M	number of grid points in spatial discretization
N	truncation point for micellar size range
R	universal gas constant
T	temperature
a_r	forward rate coefficient for the micellization process
b_r	backward rate coefficient for the micellization process
k_1, k_2	adsorption and desorption rate coefficients
p	scaling parameter for non-uniform grid formation
v	fluid point velocity
v^{∞}	fluid point velocity at x^{∞}
x^{∞}	point 'infinitely distant' from interface $x = 0$
Γ	surface concentration of adsorbed monomer
Γ^{∞}	equilibrium value of Γ
$\hat{\Gamma}$	saturated surface concentration of adsorbed monomer
Λ	subsurface concentration of monomer
Λ^{∞}	equilibrium value of Λ
α	forward rate coefficient for diffusion-limited micellization
γ	Langmuir isotherm parameter
η_r	difference between the standard chemical potentials of micelles of sizes $r+1$ and r
η_{\min}	minimum value attained by η_r
λ	characteristic length scale for monomer diffusion
μ_r	chemical potential of micelles of size r
$\bar{\mu}_r$	equilibrium value of μ_r
μ_r^{θ}	standard chemical potential of micelles of size r
ρ	total surfactant density
σ	turbulence parameter

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