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ORIGINAL CONTRIBUTION

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The flow of concentrated surfactant solutions through narrow capillaries

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Abstract The resistance of microfilters in a flow of micellar solutions indicates that the surfactant which is adsorbed in the pores forms a mobile admicelle. The flow in these admicelles can be stopped by Marangoni forces if there is a concentration gradient of surfactant across the filter. On the basis of thermodynamic concepts and experimental data it is argued that the resistance of the filters could be affected by shear-induced surfactant adsorption. To minimize the entropy production in the flow through a narrow pore the micellar solution separates into parallel fluxes of liquid through the lumen of the pore and of mobile surfactant in the flowing admicelle.

Key words Microfiltration · Admicelle mobility · Micellar solutions

Introduction

We consider the flow of liquids through narrow capillaries, such as in the pores of a microfilter or in textile fabrics during laundering. The liquids which were studied are micellar surfactant solutions. Adsorption of surfactant from such a solution on the pore walls creates a continuous bi- or multilayer of surfactant molecules (the "admicelle"), which could narrow the pore lumen through which the liquid flows. It is not known whether the adsorbed layer of surfactant remains stagnant like a solid during the flow of a viscous liquid through the pore or whether it moves along the pore walls like a layer of liquid-crystalline nature would. Moreover, it has been suggested [1–3] that the rate of shear can affect the condition of micellar solutions as an independent variable of state. In that case adsorption and phase behaviour in flowing, concentrated surfactant solutions would differ from the stagnant conditions. Properties of micellar solutions like these will manifest themselves in microfiltration. This makes flow through narrow pores of surfactant solutions with concentrations of up to 10 times the critical micellization concentration (cmc) a scientifically interesting and technologically important issue.

Theoretical concept

Let us consider flows of micellar solutions through a narrow pore with a given geometry. At a constant volumetric flux through the pore the shear rates and liquid velocities everywhere in the pore are given by the Poiseuille profile for laminar viscous flow. The pattern of velocities and shear rates remains unaltered when the liquid viscosity is changed. The liquid is incompressible, and for a constant volumetric flux of a Newtonian liquid through the pore there is a linear relation between the local liquid velocity and the pressure gradient which generates the flow.

We shall define the resistance of a pore in terms of measurable quantities. It is the ratio of the pressure difference and the (constant) volumetric flux of liquid which is caused by that pressure difference. In a microfilter membrane, as was used in our experiments, there are a large number (N) of parallel cylindrical pores per unit membrane area. A membrane like that can be modelled as a solid cylinder with a small L/D ratio, perforated with many cylindrical channels with their own, large L/d ratio (Fig. 1). The pores through the membrane are narrow, of radius a, the Reynolds number is low and the flow is laminar.

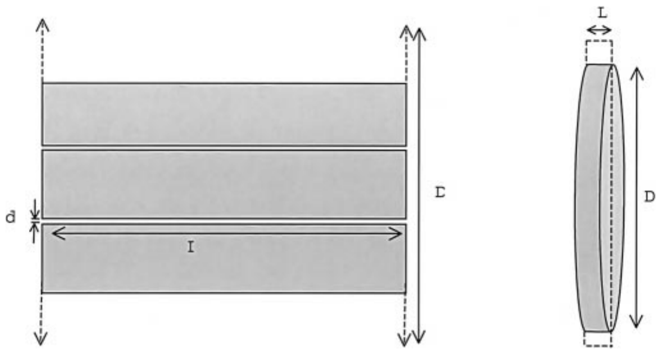


Fig. 1 Model of a radial cross-section of the membrane

If the no-slip condition holds, flow in each channel has the parabolic "Poiseuille" velocity profile:

$$v_i = \frac{(\Delta P/L)_i - \rho g}{4\eta} \cdot \left(a_i^2 - r^2\right) \; .$$

The volumetric flow rate through the membrane is the sum of the flow rates through the individual channels, which are found by integrating v_i over the cross-sectional area. The linear pressure drop over the membrane ($\Delta P/L$) is equal for all channels. Since $\Delta P/L \gg ge$

$$Q = \sum_{i=1}^{n} Q_i = \sum_{i=1}^{n} \frac{\pi a_i^4 \Delta P}{8\eta L}$$

and thus the scaled membrane conductivity, M, becomes

$$M \equiv \frac{\dot{m}v}{\Delta P} = \frac{Q\rho\eta/\rho}{\Delta P} = \text{Const}\ \frac{Na^4}{L} \quad ,$$

where $\dot{m}$ is the mass flow of the liquid through the membrane.

We have defined the pore conductivity and described it in a model; however, that does not mean that the chosen model is indeed correct. The measured quantity in an experiment is the energy dissipation of the viscous flow which follows from the the flux, Q, and the pressure drop, ΔP, across the membrane. At a constant flux (i.e. for the same Poiseuille profile) the dissipation is proportional to the viscosity of the liquid. The Poiseuille profile of liquid velocities is representative for the minimum entropy production by a viscous liquid in a stationary state of laminar flow between rigid walls. With equal flux the entropy production will be proportional to the viscosity.

The presence of micellar aggregates in a liquid augments its viscosity (Fig. 2).

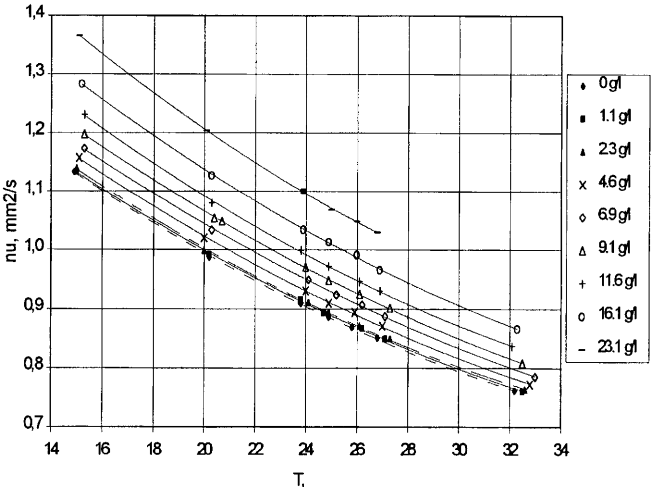


Fig. 2 Kinematic viscosity of sodium dodecyl sulfate (*SDS*) solutions as a function of temperature

Micelles consist of surfactant molecules. There is an association/dissociation equilibrium between the individual surfactant molecules and the micelles and also with layers of surfactant ("admicelles" [4]) that are adsorbed at the walls of the pore. The viscous properties of the adsorbed surfactant bi- or multilayers are not well known. It seems reasonable to assume that the molecules of these layers are "soft condensed matter". The molecules have considerable mobility, like in lyotropic liquid crystals of soap molecules or in the surface layers of soap films. As a consequence the admicelles may be dragged along by the forces which the flowing liquid exerts on the pore wall. When a flow carries away adsorbed surfactant molecules, the equilibrium must be restored by adsorption of fresh surfactant from the micellar solution.

Transport by drag on the admicelles will only be sustained if the surfactant which is flowing away can be replenished by adsorption from the micellar solution at the front end of the pore and if the influx of surfactant molecules is remicellized into the solution at the rear. Energetically, micellization and demicellization to restore the adsorption equilibrium in the dynamic situation at the pore ends must be "easy" processes. The heat of micellization in a surfactant solution at the cmc is small. The entropy production for restoring the dynamic equilibrium at the pore ends (by exchange of surfactant molecules between the admicelle and the micellar solution) is small. Most of the entropy production inherent in the surfactant transport through the admicelles will be caused by the friction inside the admicelle while it slides along the rigid pore walls.

In a steady state the entropy production is at the minimum level that is compatible with the experimental boundary conditions. This applies for all viscous fluids in flow, including micellar solutions of surfactant molecules. In micellar solutions the viscosity increases with the surfactant concentration (Fig. 2). Under conditions of constant temperature and equal volumetric flux the presence of the micelles augments the dissipation in proportion to the increment in the kinematic viscosity. It is then conceivable that the overall rate of entropy production is lowered by adsorption of extra surfactant in the admicelle. Transport of this surfactant is in the form of the thicker admicelle sliding over the pore walls. The viscosity of the liquid in the Poiseuille profile is reduced.

Given the possibility of two separate fluxes, one of the water and one in the admicelle, the optimum, minimum condition for entropy production will determine the distribution of surfactant molecules between the fluxes in the micellar solution and in the admicelle. The extra adsorption must be related to the shear rate in the micellar solution and to the surfactant concentration which determines the viscosity.

Experimental

Experimental considerations

In search of evidence for pore-narrowing by the adsorption of surfactant layers we measured the scaled conductivities, M, of microfilters. In these filters 4% of the volume consisted of uniform linear pores of 10 μm length and 0.1 μm diameter. The flow in a pore will be of the Poiseuille type, and the flow resistance follows directly from the pore dimensions and the viscosity of the liquid. Our experiments were done at a constant flux of the liquid through the membrane. Measuring the pressure drop across the filter then gives the flow resistance. By scaling that result with the kinematic viscosity one obtains M. Changes in the geometry of the pores (e.g. when they are made narrower by admicelles on the pore walls) alter the pore resistance. M discriminates between these effects and the trivial observation that the flow resistance is bigger when a more viscous liquid is forced through a pore. For a given membrane, M should remain constant for Newtonian liquids of different viscosities as long as the size and shape of the pores remain constant. When differences in M are detected in experiments they indicate changes in the pore geometry. These changes may be due to adsorption and desorption, but different M can also indicate variable slip of the flow along the pore walls. Such a conductivity change has indeed been found in investigations [5] of slipping polymer layers and in water flow over nonwettable surfaces [6]. Deviations in M at different shear rates can indicate non-Newtonian properties of the liquid. Slip in the admicelle would reveal itself in values of M which exceed the expectations for flow of the surfactant solution through a pore. In the case where the admicelle moves with the flow, the flux through a pore could be described as an extra plug-flow (for the moving "tube" of surfactant inside the pore wall) superimposed upon the Poiseuille flow of the (more dilute and less viscous) solution through the open lumen of the pore.

Experimentally, measuring M is not as straightforward as it might seem. Microfilters happen to be designed for filtering particulate matter, microorganisms, dilute polymers, etc. out of the liquids which flow through them. In the process the filters themselves become contaminated, scaled and clogged on a micro- and nanoscale. This changes the condition or the number, N, of the active pores and is then reflected as a change in M. Also, the considerable pressure drop over a microfilter may allow bubbles of dissolved gas to develop inside the pores. All in all, the condition of the filter membrane is, and remains, a variable of the experiment. It must be eliminated from the results before these can be interpreted.

Experiments

Carefully designed experiments (e.g. by using specially decontaminated ingredients and inserting a large-area prefilter between pump and measuring filter) resulted in M changing by less than 1% during 1 h constant flow of pure liquids such as water and ethanol and of surfactant solutions through the filter at fluxes of the order of 0.1 ml s^{-1}.

In these conditions a constant flux of liquid was imposed (Fig. 3). The concentration in that flux could be switched (in a few seconds) between zero (pure water) and surfactant concentrations up to 10 times the cmc. The dead time between the concentration change and the altered solution reaching the filter membrane was of the order of 100 s. The liquid flux, $\dot{m}$, and the pressure drop, ΔP, across the membrane were monitored continuously.The resulting M would reach a new steady-state value some time after the concentration change. In each experiment this value was compared with M for the pure solvent (water), determined by switching back to that solvent (i.e. to zero surfactant concentration) and keeping the liquid flux constant without interrupting the flow. In this fashion, a series of experiments was carried out (Fig. 4), each consisting of measuring M for a new solution with another concentration and comparing the result with that for the pure solvent which was measured before and afterwards. The procedure allowed M to be compared for different surfactant concentrations, temperatures, ionic strengths, pH values, etc., so that timescales and magnitudes of processes and effects in the pore conductivity could be established.

In the apparatus of Fig. 3 the mass flow rate was determined using a Sartorius balance (BP 2100S) and a data-acquisition program (Lucy 3.7.5, Kievit Tech Consult): the total effluent weight was sampled every 10 s and the resulting time series was differentiated to arrive at the mass flow rate. The pressure drop was measured with an electronic Bronkhorst Hi-Tec pressure meter (type P-502C-FA-39-V; read-out E 7500-AAA) linked to a dynamic data-exchange program (RS232/Flow Bus interface; FlowDDE software) to produce a time series (in Microsoft Excel). As for the mass, the pressure was sampled every 10 s. The solutions were pumped (Micropump 75225-05/184-00-010) from vessels with heating jackets connected to thermostatic baths (Tamson TC3/TCL3); therefore, temperature variations were small and automatic sampling was not required. The temperature was measured using a thermocouple. Samples for determining the viscosity were taken without disturbing the mass flow measurement. The kinematic viscosity was determined with a capillary viscometer (Tamson Ubbelohde OC). The sodium dodecyl sulfate (SDS) solutions were Newtonian fluids for which there was no detectable change in the viscosity with the rate of shear in a Couette viscometer (Contraves LS 40). Solutions of SDS were prepared with "double-distilled" water and SDS ("for biochemistry and surfactant tests") supplied by Merck. The cmc of SDS at standard temperature and pressure is approximately 2.4 g/l. Using SDS as a surfactant, experiments were done at solution concentrations of between 0.5 and 10 times the cmc. All experiments were done at temperatures well above the Krafft temperatures at these concentrations [7] in order to avoid surfactant crystallization phenomena. The membrane filters used

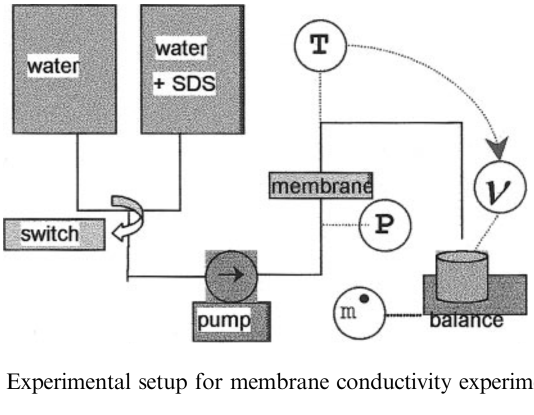


Fig. 3 Experimental setup for membrane conductivity experiments

for the experiments were polycarbonate membranes hydrophilized with a poly(vinylpyrrilidone) coating (Isopore; VCTP 0.1 μm Millipore). Before and after the experiment membranes were compared in Scanning electron microscope (SEM) micrographs. The membrane specifications were membrane diameter 25 mm, maximum pore diameter 0.1 μm, porosity 4% void volume/total volume, membrane thickness 10 μm.

Results

The results of a typical run of experiments are shown in Fig. 4. The steady-state values for *M* of the membrane in this experiment were 0.126 at 10 cmc, 0.134 at 5 cmc, 0.136 at 2 cmc, 0.137 at 1 cmc and 0.138 for pure water. The absolute values here are not relevant; they represent one specific membrane at a given temperature and flow rate. From the definition of *M* there is a viscosity correction in these conductivity data. It is clear that the steady-state value of *M* decreases with increasing surfactant concentration, and this is a common feature in all the measured data with SDS solutions. We are not alone in this observation either [8]. Analogous phenomena were seen in another laboratory, with completely different apparatus being used for the microfiltration and purification of SDS solutions. That *M* decreases with increasing surfactant concentration is a property of concentrated SDS solutions flowing in narrow pores. If *M* decreases with increasing surfactant concentration this implies that there is some concentration-dependent obstruction, such as an adsorbed bilayer or admicelle, which reduces the lumen of the pores.

A second observation, which is illustrated by Fig. 4, is the asymmetry in the time to reach the steady-state value of *M*. A distinctly asymmetrical pattern developed at concentrations of 1, 2 and 5 cmc. When a more concentrated solution arrives at the membrane, it takes a minute or less for the scaled conductivity to settle to the new, lower steady-state value; however, upon dilution of the surfactant the scaled conductivity first drops to an even lower value. It takes more than 1 h before the higher steady-state value for the low surfactant concentrations is reached.

The relative decrease in the pore size can be calculated from the experimental values of the conductivity and the variation in the thickness of the admicelles with the surfactant concentration can be calculated from the actual size of the pores. The result of such a calculation is shown in Fig. 5.

It is seen that the effective thickness of the admicelles increases with the surfactant concentration. As such, this is not a strange effect, although somewhat unexpected in view of the measured adsorption isotherms [9]. These seem to indicate that bilayers of a constant thickness (of approximately 2 nm) cover the pore walls at these SDS concentrations. Before we did the experiment, we thought that either this would be found or stratified multilayers would build up (in steps of 2 nm) at the higher concentrations. It was unexpected to find that the flow would be impeded by admicelles of less than a monolayer's thickness.

One might, of course, think that the small admicelle thicknesses in Fig. 5 are an artifact, for example, because we have assumed one pore diameter. A broad distribution of real pore sizes would give an exaggerated contribution of the larger pores in a flow experiment and so reduce the relative size of the admicelle; however, such an explanation was neither corroborated by the SEM observations nor could explain why the thickness of the admicelles (supposedly constant at 2 nm) should become concentration-dependent in the calculated result.

Small values of the admicelle thickness, as in Fig. 5, could indicate mobility of the surfactant molecules in the adsorbed layer. Slip of the flow along the pore walls reduces the overall pore resistance. Real admicelles may be thicker than calculated in Fig. 5, if they flow through the membrane with the liquid.

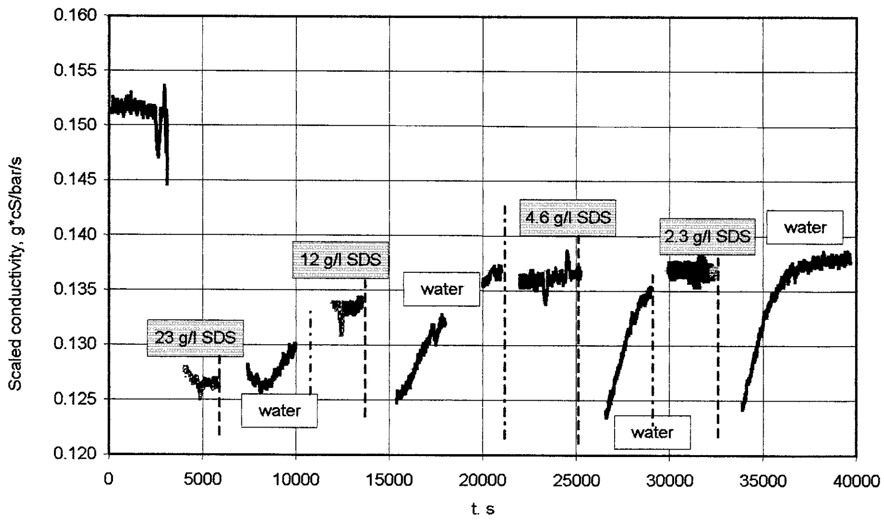
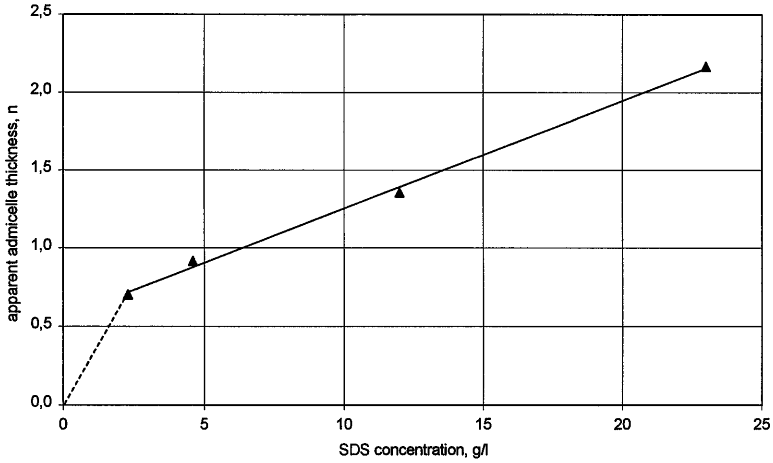


Fig. 4 Conductivity of a membrane measured at a constant flux for water and for SDS solutions of different concentrations

Fig. 5 Apparent admicelle thickness as a function of SDS concentration. Assumed pore radius $a = 50$ nm



Discussion

A micellar solution has two different options for the transport of a surfactant through a pore. The surfactant can be carried along in the viscous liquid, which moves through the pores in Poiseuille flow. The price paid in this mechanism of surfactant transport is the extra entropy production because of the increased fluid viscosity. The alternative is that surfactant molecules move through the pore in a slipping admicelle which is dragged through the pore by the Poiseuille flow. The depleted liquid itself now has a low viscosity. The second mechanism implies extra entropy production for demicellization at the front end of the pore, for micellization of the surplus of surfactant at the rear and for slip in the admicelle which covers the pore wall. The entropy production in the Poiseuille profile is lower in this case. The reduced values of the admicelles' thicknesses inside the conducting pores are not the only argument for slip in the adsorbed surfactant layer. Mobility of the surfactant can also explain why the pore conductivity decreases when the surfactant solution is diluted (Fig. 4). We have noticed the asymmetry in the relaxation rate of the measured conductivity after changes in surfactant concentration. When the concentration was diluted from a surfactant solution to pure water, it took a long to come to the eventual steady state and, even more surprising, in spite of the dilution, the value of M drops instantaneously instead of increasing. Dilution at constant flux gives an extra pressure difference, $\Delta P'$, across the membrane. The effect cannot be of an osmotic nature: it has the wrong sign to begin with. The observations are not due to slow mixing either: there would be no asymmetry than between increasing and decreasing concentrations. After a concentration change, positive or negative, the immediate response is a lowering of the membrane conductivity. This is a real effect.

Mobility

Because of the mixing in the pump and during the dead time the liquid which flows through the pores immediately after the dilution may have a somewhat lower surfactant concentration, but it still resembles the original surfactant solution in concentration and viscosity. Nevertheless, the response of the membrane permeability is rapid and complete. What is affected by the dilution in front of the pores is the capacity of the solution for replenishing the surfactant in the admicelle. Inside the pore, surfactant is dragged along by the Poiseuille flow and it redissolves in the solution at the other side of the membrane. The immediate effect of the concentration gradient across the membrane is that a surface tension gradient spreads along the walls of the pores upon dilution. This is a force which counteracts the drag of the flowing liquid. Because of that surface tension gradient we interpret the sudden decrease in M as a Marangoni effect in the mobile admicelles. In this vision the difference in M between the steady state in a concentrated micellar solution and moments after dilution does not depend on the surfactant concentration in the solution or on the thickness of an obstructing admicelle but on the concentration gradient over the membrane thickness, L. In the steady state the admicelle flows with the liquid in the pore; however, a concentration gradient of the surfactant generates a Marangoni force in the admicelle which, upon dilution, works in the opposite direction of the liquid flow. This force is strong enough to compensate the drag force.

In the steady state there was a flow of surfactant inside the admicelle, but that flow will stop instantaneously upon dilution. When the experimental results are interpreted in this way, the smaller conductivity of a pore which is seen shortly after the dilution is proof of the mobility of the surfactant in the admicelle.

Admicelle thickness

When the admicelle moves with the steady-state flow and when it is stopped by a Marangoni effect, the liquid in the Poiseuille profile fills 96% by volume of the pore. In the case of the moving admicelle there must be adsorption and desorption in the steady state so that the surfactant concentration in the flow is reduced. When the flow of the admicelle is stopped the mass balance of the surfactant which passes through the pore demands that all the surfactant molecules remain dissolved. In the first case, one might assume that the viscosity is that of the solvent water; in the second it is the viscosity of the solution (Fig. 2). The difference in the conductivities of the membrane immediately after dilution and when the undiluted solvent flows through the same pores, both compared with the steady-state conductivity for water, can be used to calculate the real thickness of the admicelle. Upon dilution the adsorbed layer is kept in position as an obstruction by the Marangoni force. In the steady state it moves along because of the viscous drag exerted by the liquid. Calculation along these lines leads to an estimated thickness of the stagnant admicelle of the order of 2 nm, just as would be expected for a surfactant bilayer.

In our experiment the flux of the surfactant solution through the pores is constant. Independent of the model this implies that the transport of surfactant molecules through a cross-section of a pore varies in proportion to the surfactant concentration in the solution. Now, let us assume that practically all the surfactant passes through the pore in the moving admicelle layer. The drag force on the admicelle will then be as with water flowing by, irrespective of the original surfactant concentration. Also, there is no reason why the friction of the admicelle should depend on the surfactant concentration outside the pore. An admicelle will slide as an undisturbed liquid crystal. It has a relatively high viscosity and a velocity that is independent of the surfactant concentration. Because transport of the surfactant must remain proportional to this concentration, the thickness or the density of the moving admicelle becomes proportional to the concentration. Shear in a micellar solution, when it flows through a narrow pore, must indeed lead to increased adsorption. This is a consequence of the surfactant balance in the flow.

Entropy production

The final question to be addressed is whether the principle of mimimum entropy production allows separation of a micellar liquid into two parallel, separate fluxes: of the solvent and of the surfactant. The solvent is a more diluted liquid with a lower viscosity and the surfactant flux is concentrated in liquid-crystalline admicelles which slide over the pore walls. In other words: is it possible that the separation of fluxes reduces the rate of entropy production in the flow through the pore? The total energy dissipation in the separate fluxes must be compared with that in a micellar solution (with its original viscosity) flowing through pores with fixed walls.

These are exactly the two situations which we have described as the steady-state flow for a surfactant solution and the flow of that same solution immediately after the admicelle has been stopped by a Marangoni force, respectively. In both cases the pore walls will be covered with a surfactant bilayer of the order of 2-nm thickness. In one mechanism the bilayer is fixed on the walls and contributes nothing to the entropy production. All dissipation in the pore is in the Poiseuille flow of the micellar solution. In the second case the bilayer is in flow. It experiences the friction of the rigid pore wall and needs micellization and demicellization processes at the surfaces of the membrane. The thickness of the flowing admicelle must be proportional to the surfactant concentration. The liquid has a lower concentration because of the extra shear-induced adsorption in the admicelle. The total entropy production in the two cases is found by comparing scaled conductivities: in the steady state and immediately after the admicelle flow has been stopped by the Marangoni force.

Let us reconsider our experimental results (Figs. 4, 5) with the model of the sliding admicelle in mind. In fact, these data compare energy dissipation of different micellar solutions which flow through the same set of pores. The presence of the micelles led to larger dissipation as the surfactant concentration increased, but the scaled conductivity data were already corrected for the viscosity. In the original assumption each liquid flows through the pore with unchanged viscosity and this flow is obstructed by a fixed admicelle layer. This adsorbed layer reduces the available pore radius to a somewhat smaller a_{eff}. From the difference in the scaled conductivities during the steady state and immediately after dilution and multiplying by the kinematic viscosities of the liquids as discussed previously, we have, in principle, measured the dissipation of energy in the two situations. It is clear at a glance that the entropy production must have been smaller in the steady-state situation than when the flow of the admicelle was stopped by a surface tension gradient.

Figure 5 presented the calculated thicknesses of the obstructing layer as the difference between a and a_{eff} in the original model. On the other hand, measured adsorption data [4] suggest that in all the solutions the equilibrium thickness of the admicelle is the same: of the order of 2 nm for an SDS bilayer. Dissipation in a Poiseuille flow is proportional to the viscosity and to a^{-6} at equal fluxes. What Fig. 5 shows is that the energy dissipation in all cases is smaller than that which would correspond to the real admicelle obstructing the flow of the unchanged solutions. The dissipation increases with the concentration. This is what would be expected. In these steady states the rates of demicellization and micellization as well as the transport in the admicelle must remain proportional to the surfactant concentration; however, as long as energy dissipation by separate fluxes remains smaller than with a fixed layer the total flux of the solution through the pore must split into two separate, parallel flows of water and of surfactant. Minimization of the entropy production drives the extra adsorption of surfactant molecules in the admicelle under the influence of shear.

Conclusion

Measurements on the resistance of microfilters in a flow of micellar solutions of SDS indicate the mobility of the surfactant layers which are adsorbed on the walls of the filter pores. The apparent thickness of the adsorbed layers is smaller than that of a surfactant bilayer. This can be explained if the bilayer flows with the liquid through the pore, rather than obstructing it. Flow of the surfactant in the adsorbed layers is stopped by Marangoni forces if there is a gradient in the surfactant concentration across the filter.

In a steady-state flow of a micellar solution through a microfilter pore there will be enhanced surfactant adsorption on the pore walls because of the shear in the solution. The shear-dependent adsorption is a consequence of the minimization of the entropy production. A micellar solution separates into parallel fluxes, one of low viscosity (solvent) and the other a concentrated, liquid-crystalline admicelle, to minimize the energy dissipation of the viscous flow through a narrow filter pore.

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