Diffusion in the Micellar and Hexagonal Phases of the $C_{12}EO_6/H_2O$ Mixture: A Directional-Growth Study

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Abstract. — We studied in directional growth the Mullins-Sekerka instability at the interface between the hexagonal H_α phase and the micellar phase of the lyotropic mixture $C_{12}EO_6$ +water. We first worked at the azeotropic concentration (50wt% of surfactant). When the $C_{12}EO_6$ is pure, the mixture behaves as a pure compound and the Mullins-Sekerka instability disappears. It reappears when the soap degrades by radical oxidation in the presence of light and heat. We measured as a function of impurity concentration and of column orientation, the critical velocity, wavelength, and drift velocity in growth and in melting. From these experimental data, we deduced the mean diffusion coefficients of impurities in the micellar phase (D_L^i) and in the hexagonal phase, parallel ($D_{||}^i$) and perpendicularly ($D_{\perp}^i$) to the molecular columns. We then shifted a bit from the azeotropic concentration, taking care to avoid surfactant degradation. Similar experiments in growth and in melting allowed us to determine the three diffusion coefficients D_L , $D_{||}$ and $D_{\perp}$ of the surfactant concentration field. The values found differ from the values obtained for impurities and are compared to the individual diffusion coefficients of the water and of the $C_{12}EO_6$ measured by NMR. Finally, we measured the kinetic coefficient for molecular attachment at the interface. We found that kinetics are linear and symmetrical in growth and in melting.

Résumé. — Nous avons étudié en croissance directionnelle l'instabilité de Mullins-Sekerka à l'interface entre la phase hexagonale H_α et la phase micellaire du mélange lyotrope $C_{12}EO_6$ +eau. Nous avons d'abord travaillé à la concentration azéotrope (50% de surfactant en poids). Lorsque le $C_{12}EO_6$ est pur, le mélange se comporte comme un corps pur et l'instabilité de Mullins-Sekerka disparaît. Elle réapparaît lorsque le savon se dégrade par oxydation radicalaire à la lumière et à la chaleur. Nous avons mesuré en fonction de la concentration en impuretés et de l'orientation des colonnes moléculaires, la vitesse critique, la longueur d'onde et la vitesse de dérive des cellules en croissance et en fusion. De ces données expérimentales, nous avons déduit les trois coefficients de diffusion moyens des impuretés dans la phase micellaire (D_L^i) et dans la phase hexagonale, parallèlement ($D_{||}^i$) et perpendiculairement ($D_{\perp}^i$) aux colonnes moléculaires. Nous nous sommes ensuite écartés légèrement de la concentration azéotrope en prenant soin d'éviter la dégradation du surfactant. Des expériences analogues en croissance et

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en fusion nous ont permis de déterminer les trois coefficients de diffusion D_L , $D_{||}$ et $D_{\perp}$ du champ de concentration en surfactant. Les valeurs trouvées diffèrent de celles obtenues pour les impuretés et sont comparées aux coefficients de diffusion individuels de l'eau et du $C_{12}EO_6$ mesurés par RMN. Enfin, nous avons mesuré le coefficient cinétique d'attachement moléculaire à l'interface. Nous avons trouvé que la cinétique est linéaire et symétrique en croissance et en fusion.

1. Introduction

Metallurgists have long known that the front between a crystal and its melt is unstable above some critical velocity in directional solidification. This instability, first analyzed in detail by Mullins and Sekerka [1], is usually caused by the rejection of solute atoms (impurities, most often) from the solid into the liquid, where they pile up in front of the moving interface. More precisely, the concentration field of the solute is destabilizing, whereas surface tension and temperature gradient are stabilizing. From this competition result a critical velocity and a critical wavelength which can be predicted from a linear-stability analysis of the front. Experimentally, this instability is mostly observed during the growth of the crystal. Conversely, its observation in melting, although theoretically possible, is more difficult as it is often concealed by the nucleation of liquid germs in front of the moving interface. As explained by Woodruff [2], nucleation often occurs because the interface is completely stable while extensive regions of constitutional superheating are present. Also, the smaller the diffusion coefficient in the liquid in comparison with the diffusion coefficient in the solid, the larger this effect. This explains why the Mullins-Sekerka instability is easier to observe in melting in liquid crystals (like nematics for instance [2]) than in usual materials like metals or plastic crystals.

In general, physicists are interested in the nonlinear evolution of growth patterns which develop above the onset of instability. From this point of view, liquid crystals prove to be very interesting because they allow the study of various problems such as secondary instabilities of cellular fronts [3], dendrites [4] and morphological transitions between different growth regimes [5]. Directional growth of liquid crystals can also be useful for determining some bulk and surface properties of the system chosen. One example is the determination of the diffusion coefficients of a solute in the two phases in contact. This method gives good results providing there is no convection in front of the moving interface. For instance, measurements in directional growth of diffusion coefficients in thermotropic columnar mesophases [6] are in good agreement with direct measurements performed by Daoud *et al.* [7]. By contrast, convection in front of a moving nematic-isotropic interface can lead one to overestimate diffusion coefficients by many orders of magnitude [8]. The attachment kinetic coefficient can also be found from directional solidification by measuring the front temperature as a function of its velocity [9,10].

In this article, we study the destabilization in directional solidification of the hexagonal-micellar front of the $C_{12}EO_6/H_2O$ system and we show that this technique can give valuable information on both attachment kinetics and diffusion in the two phases. In particular, we shall see that this method complements pulse-field gradient NMR, in that the former gives collective diffusion coefficients while the latter gives individual diffusion coefficients of the surfactant and of the water.

We recall that the non-ionic surfactant $C_{12}EO_6$ is the hexa-ethylene glycol mono-n-dodecyl-ether or $CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$. It was obtained from Nikko Chemicals Co., Ltd and was used without further purification. Its whole phase diagram (Fig. 1) [11] shows that there exists an azeotropic point between the direct hexagonal phase H_α and the micellar isotropic

Fig. 1. — Full phase diagram of the $C_{12}EO_6/H_2O$ mixture (from Ref. [11]).

liquid for a composition of about 50 wt% of $C_{12}EO_6$.

We have chosen to work nearby this point for two reasons:

- first, the mixture behaves exactly as a pure compound at the azeotropic concentration. Consequently, the Mullins-Sekerka instability is expected to disappear at this concentration, which should facilitate the measurement of the kinetic coefficient. Such a measurement should help to better understand this phase transition in the future;
- second, there are theoretical calculations by Misbah [12] on the Mullins-Sekerka instability in quasi-azeotropes which will be very useful to interpret our experimental data.

In addition, this lyotropic system is expected to be very anisotropic because of its columnar structure. It is thus a good system for exploring the influence of diffusion anisotropy on the cellular bifurcation.

We also recall that planar monodomains of the hexagonal phase of this mixture can be obtained in directional solidification [10], which will be essential for measuring the diffusion coefficients parallel and perpendicularly to the columns.

The plan of the article is the following: in Section 2, we show the precise phase diagram of the $C_{12}EO_6/H_2O$ mixture near the azeotropic concentration and that of the $C_{12}EO_6/H_2O$ mixture at the azeotropic concentration in the presence of impurities. In Section 3, we show that the cellular instability completely disappears at the azeotropic concentration and we determine the molecular attachment kinetic coefficient. In Section 4, we examine the case of an impure azeotropic mixture and show how to determine the three mean diffusion coefficients of the impurities. Section 5 is devoted to quasi-azeotropic pure mixtures (*i.e.* free of impurities as much as possible). In this case, the front instability is due to the destabilizing effect of the concentration field of the surfactant itself. We shall see that this experiment gives access to the hydrodynamical mass diffusion coefficients in the two phases. Finally, we compare in Section 6 these diffusion coefficients with the individual diffusion coefficients of the water and of the surfactant given by NMR.

Fig. 2. — Enlargement of the phase diagram near the azeotropic point.

2. Phase Diagrams

Before performing any experiment of directional growth, it is crucial to determine accurately the phase diagram of the chosen mixture and to test its chemical stability.

For this purpose, we prepare mixtures at different concentrations and measure their solidus and liquidus temperatures. Samples are prepared between two glass plates and are filled by capillarity in a moist atmosphere. They are then sealed with an epoxy glue (Epotecn Luxtrak LCR 0208). Their thickness ranges between 40 and 180 μm although most of our experiments were done with 75 μm thick samples. To measure the solidus and liquidus temperatures, we place the sample into an oven. The temperature is regulated to ± 5 mK and the temperature gradient within the sample is less than 0.01 K/cm. The sample is observed through a polarizing microscope between crossed polarizers. Measuring the freezing range must be done carefully, by changing slowly the temperature in order to remain as close as possible to equilibrium. The procedure is the following: we first set the sample at a temperature where the two phases coexist; we then heat the sample till the last germ of hexagonal phase disappears: this gives the liquidus temperature. As for the solidus temperature, it is obtained by decreasing the temperature till complete disappearance of the isotropic liquid. Let us emphasize at this stage that heating the completely crystallized hexagonal phase till nucleation of isotropic liquid germs, leads, in general, one to overestimate the solidus temperature. Indeed, it is often possible to superheat the hexagonal phase by a few tenths of a degree. We will return to this point when we discuss the Mullins-Sekerka instability. An enlargement of the phase diagram near the azeotrope is shown in Figure 2. As expected, the measured freezing range vanishes at the azeotrope (in practice, impurities lead to a minimum freezing range of the order of 0.01 $^{\circ}\text{C}$). Thus, there is no difference in concentration between the two phases at this point, which means that the mixture behaves as a pure compound (as long as impurities may be neglected, which is the case in fresh samples). We also see in Figure 2 that solidus and liquidus lines can be fit to quadratic laws:

$$T_{L,S} - T_{0L,S} = \alpha_{L,S}(C_{L,S} - C_0)^2 \quad (1)$$

with

$$T_{0L} \approx T_{0S} \approx 38.85^\circ\text{C} \quad C_0 \approx 50\% \quad \alpha_L = -325.7^\circ\text{C} \quad \alpha_S = -496.7^\circ\text{C}$$

In these formulas, the subscripts L and S denote the liquidus and solidus lines, while the subscript 0 refers to the azeotropic point. With these values, we calculate $K' \approx 0.81$, where K' is the equilibrium concentration distribution coefficient defined to be:

$$K' = \sqrt{\frac{\alpha_L}{\alpha_S}} \quad (2)$$

In order to estimate the degradation velocity of the surfactant, we prepared 10 tubes, each of them containing 5 cm³ of the mixture C₁₂EO₆ + H₂O at different concentrations near the azeotropic one. We then measured their solidus and liquidus temperatures regularly over one year. Of course, we took care that the tubes containing the mixtures were tightly sealed in order to prevent water evaporation. On the other hand, they were kept at room temperature and were intentionally not protected from light. Our results are shown in Figure 3a for the tube at the azeotropic concentration as a function of time. In this figure, we assumed that all the measured liquidus temperatures lie on the same straight line. This assumption is reasonable insofar as the solidus is a straight line, too. Here, the x -axis represents impurity concentration. This phase diagram shows that the impure azeotropic mixture behaves as a dilute binary mixture whose effective partition coefficient of the impurities $K \approx 0.93$. In Figure 3b, we show the full phase diagram measured after 2 months. A comparison to Figure 2 shows that both the solidus and the liquidus lines shifted down and no longer touch at their apices. We emphasize that the minimum freezing range was obtained with the tube that was initially at the azeotropic concentration. This clearly shows that our samples did not dry during the whole duration of our experiments.

Where do the impurities come from? A few possible mechanisms of degradation are given in reference [13]. Our product is composed of one alkyl group with 12 carbon atoms, 6 ethyloxy groups (O-CH₂ or EO in brief), and one hydroxyl group OH. Its chemical formula can thus be rewritten in the form R-O-CH₂-R' where R is the alkyl group, plus possibly a few ethyloxy groups, and R' one or several ethyloxy groups and the hydroxyl group. In the following synopsis, we show a few possible reactions leading to the degradation of the surfactant by oxidation of the polar head:

Thus, oxidation of the ethyloxy group gives a series of derivative products. Because the degradation can simultaneously occur on many EO's, the degradation of the C₁₂EO₆ can lead to several chemically different molecules. Because oxidation by O₂ is initiated by light and by

Fig. 3. — a) Phase diagram of the azeotropic mixture (50 wt% of $C_{12}EO_6$ in water) in the presence of the impurities coming from the degradation of $C_{12}EO_6$. The impurity concentration C is given in arbitrary unit (1 in this unit would correspond to 10^{-6} mole/cm³ by assuming that the Van't Hoff law is applicable). b) Phase diagram near the azeotrope after 2 months.

heat, we stored all our samples away from light in the freezer at +4 °C. In this way, it is possible to keep the same mixture during a few months without visible degradation.

In the following section, we discuss attachment kinetics at the interface.

3. Attachment Kinetics at the Azeotropic Concentration

Because the freezing range at the azeotrope is very small, we expect the critical velocity to diverge at this concentration. We indeed observed that the front is stable in a large range of

Fig. 4. — Double sample used for measuring the front temperature.

pulling velocities between $-80 \mu\text{m/s}$ (melting front) and $80 \mu\text{m/s}$ (freezing front). For larger velocities, nucleation occurs ahead of the interface, which is no longer well-defined. Our samples are $50 \mu\text{m}$ -thick and are grown in the directional-growth apparatus described in reference [10]. They are prepared in planar orientation with the columns parallel to the front, using the method given in [10]. In order to measure the front temperature as a function of its velocity, we used the double-sample method described in reference [9]. It consists in superimposing our planar sample of hexagonal phase and a homeotropic sample of the mixture 8CB-10CB (0.76% and 0.24% in weight respectively) (Fig. 4). This mixture of classical cyanobiphenyl liquid crystals has a nematic-smectic A phase transition at 38.8°C very close to the hexagonal-micellar transition temperature of our mixture at the azeotrope. Furthermore, we know from previous measurements of Cladis *et al.* [14] that the attachment kinetics are very fast at the nematic-smectic front, so that its temperature is constant and independent of the pulling velocity. Thus, the front temperature is measured by locating through the microscope the position of the two fronts. Let $\Delta d_1(V)$ be the shift between the two fronts at velocity V . This measurement must be corrected for the small shift $\Delta d_2(V)$ that comes from the inevitable vertical temperature gradient within the sample. This latter can be easily measured by superposing two reference samples. The kinetic undercooling (or superheating) δT_{kin} is thus given by:

$$\delta T_{\text{kin}} = G[(\Delta d_1 - \Delta d_2)(V) - (\Delta d_1 - \Delta d_2)(V = 0)] \quad (3)$$

where G is the temperature gradient (of the order of 40°C/cm) which we measured with a thermocouple in a dummy sample in freezing and melting for each velocity.

Experimental results when the columns are parallel to the front are shown in Figure 5. Within experimental errors, kinetics are linear without visible asymmetry between melting and freezing fronts, which means that wetting effects are negligible [14b]. Let μ be the kinetic coefficient defined to be:

$$\delta T_{\text{kin}} = V/\mu \quad (4)$$

The best fit of experimental data to a linear law gives:

$$\mu \approx 210 \pm 40 \mu\text{m/s/K}$$

Let us emphasize that we found the same value after varying the sample thickness from 40 to $100 \mu\text{m}$. This means that the latent heat release is negligible and not responsible for the

Fig. 5. — Kinetic undercooling (resp. superheating) *versus* freezing (resp. melting) velocity.

observed shift of the front. Another way to show that latent heat is negligible is to check the inequality [15]:

$$\frac{Ld\mu}{\kappa_v} \ll 1 \quad (5)$$

where L is the latent heat per unit volume ($L \approx 1.2 \times 10^7$ erg/cm³ [16]), d the sample thickness and κ_v the thermal conductivity of the glass ($\kappa_v \approx 10^4$ erg/cm/s/K). In our experiment $\frac{Ld\mu}{\kappa_v} \approx 0.1$ by taking $d = 50$ μ m so that inequality (5) is reasonably well-satisfied.

We also tried, without success, to measure the kinetic anisotropy by rotating the sample within the temperature gradient, which we can do easily with our experimental set up [10]. Unfortunately, these experiments are tricky because of the tendency of columns to spontaneously reorient perpendicular to the temperature gradient at freezing fronts whereas nucleation disturbs the front during melting. Measurements are also too noisy to see any significant variation of the kinetic coefficient. Nevertheless, we can conclude that the kinetic anisotropy is less than 0.2 at small velocities ($V < 50$ μ m/s).

In the following section, we discuss the Mullins-Sekerka instability in the impure azeotropic mixture.

4. Mullins-Sekerka Instability in the Impure Azeotropic Mixture

We have seen that the C₁₂EO₆ slowly degrades in time. In order to study the effect of impurities on the destabilization of the front in directional solidification, we used the azeotropic mixture, which we know to behave as a pure compound in the absence of impurities and like a dilute binary mixture otherwise (see the phase diagram in Fig. 2a). In this case, impurities pile up in front of the interface and cause instability. The critical velocity then depends on the freezing range ΔT of the sample as well as on the angle θ between the columns and the interface (Fig. 6). This angle also equals the angle between the striations and the temperature gradient

Fig. 6. — Definition of angle θ at the hexagonal-micellar interface.

G . We recall that the striations are due to an undulation of the columns [17] and are easily seen between crossed polarizers, which allows us to determine very easily the column orientation. We also know from previous studies in liquid crystals that diffusion coefficients may be of the same order of magnitude in the two phases. Thus, we must take into account the diffusion in the two phases as well as its anisotropy that we expect to be large in the hexagonal lyotropic phase. In the following, we call D_L^i the impurity diffusion coefficient in the micellar phase and $D_{||}^i$ (resp. $D_{\perp}^i$) the diffusion coefficient parallel (resp. perpendicularly) to the columns in the H_a phase.

Let us first recall the main theoretical results of the linear stability analysis.

4.1. CRITICAL VELOCITY AND CELLULAR DRIFT: THEORETICAL PREDICTIONS. — In liquid crystals, diffusion anisotropy must be taken into account in the calculations. This anisotropy breaks the mirror symmetry and generically leads to a cellular drift at the onset of instability. This drift was first observed by Melo and Oswald [17] at the smectic A-smectic B interface when the smectic B plastic crystal is growing into the anisotropic smectic A phase. More recently, Valance and Misbah [18] have shown that there is a cellular drift too when an anisotropic phase is growing into an isotropic liquid. Thus, we expect there will be a cellular drift at melting and freezing fronts when the columns make an angle θ different from 0 and $\pi/2$ with the interface.

In the following we shall write the front oscillation in the form

$$z_i = \varepsilon e^{ikx} e^{\sigma t} \quad (6)$$

where k is its wavevector and $\sigma = \sigma_R + i\sigma_I$ its complex growth rate. In this expression σ_R is the growth rate of the instability (there is instability when $\sigma_R > 0$) while σ_I is related to the drift velocity V_d of the undulation *via* the relation:

$$\sigma_I = -kV_d \quad (7)$$

Standard perturbation calculations give the dispersion relations for freezing and melting fronts. In the former case ($V > 0$, freezing), we obtain:

$$\begin{aligned} 2\sigma\Delta T = & (G + d_0 T_0 k^2 - \Delta T \frac{V}{D_L^i})(V - \sqrt{V^2 + 4(D_L^i)^2 k^2 + 4D_L^i \sigma}) \\ & - K(G + d_0 T_0 k^2)(V + \sqrt{4(D_S^i)^2 k^2 + V^2 + 4D_{12}^i kV + 4D_{22}^i \sigma}) \end{aligned} \quad (8)$$

while in the latter ($V < 0$, melting):

$$\begin{aligned}\sigma K 2\Delta T &= (G + d_0 T_0 k^2)(V - \sqrt{V^2 + 4(D_L^i)^2 k^2 + 4D_L^i \sigma}) \\ &\quad - K(G + d_0 T_0 k^2 + \frac{\Delta T V}{D_{22}^i})(V + \sqrt{4(D_S^i)^2 k^2 + V^2 + 4D_{12}^i i k V + 4D_{22}^i \sigma}) \\ &\quad - i 2k V K \Delta T \frac{D_{12}^i}{D_{22}^i}\end{aligned}\quad (9)$$

with:

$$\begin{aligned}D_{11}^i &= D_{||}^i \cos^2 \theta + D_{\perp}^i \sin^2 \theta \\ D_{22}^i &= D_{||}^i \sin^2 \theta + D_{\perp}^i \cos^2 \theta \\ D_{12}^i &= D_{21}^i = (D_{||}^i - D_{\perp}^i) \cos \theta \sin \theta \\ D_S^i &= \sqrt{D_{||}^i D_{\perp}^i}\end{aligned}\quad (10)$$

These two dispersion relations allow us in principle to calculate the onset of instability by writing that:

$$\sigma_R = 0 \quad \text{and} \quad \frac{\partial \sigma_R}{\partial k} = 0 \quad (11)$$

Finding analytical expressions for both critical and drift velocities is impossible without some simplifying assumptions. So, we shall assume in the following that *the wavelength is smaller than the diffusion length* in the two phases. This condition, which must be checked *a posteriori*, implies that:

$$k \gg \frac{V}{2D_L^i}, \quad k \gg \frac{V}{2D_S^i} \quad (12)$$

In this case, equations (8) and (9) become respectively after separating real and imaginary parts:

$$\sigma_I 2\Delta T = -K(G + d_0 T_0 k^2) V \frac{D_{12}^i}{D_S^i} \quad (V > 0) \quad (13a)$$

$$\begin{aligned}\sigma_R 2\Delta T &= GV(1 - K) - \frac{V^2 \Delta T}{D_L^i} + 2k[V \Delta T - G(D_L^i + K D_S^i)] + d_0 T_0 V k^2 (1 - K) \\ &\quad - 2d_0 T_0 k^3 (D_L^i + K D_S^i) \quad (V > 0)\end{aligned}\quad (13b)$$

and

$$\sigma_I K \Delta T = -K \left(G + d_0 T_0 k^2 + \frac{\Delta T V}{D_{22}^i} \right) \frac{D_{12}^i V}{2D_S^i} + k \frac{D_{12}^i}{D_{22}^i} V K \Delta T \quad (V < 0) \quad (14a)$$

$$\begin{aligned}\sigma_R K \Delta T &= GV \frac{(1 - K)}{2} - \frac{K \Delta T V^2}{2D_{22}^i} - k[G(D_L^i + K D_S^i) + K \Delta T V \frac{D_S^i}{D_{22}^i}] \\ &\quad + d_0 T_0 V \frac{(1 - K)}{2} k^2 - k^3 d_0 T_0 (D_L^i + K D_S^i) \quad (V < 0)\end{aligned}\quad (14b)$$

Using equations (11) and (7), we can now calculate the critical velocities and wavelengths and the corresponding drift velocities.

For freezing fronts ($V > 0$) we find:

$$V_f = \frac{(D_L^i + K D_S^i)G}{\Delta T} \quad (15)$$

$$k_f = \left(\frac{K(D_L^i + D_S^i)G^2}{\Delta T D_L^i 4d_0 T_0} \right)^{1/3} \quad (16)$$

$$V_{df} = \frac{K G V_f (D_{||}^i - D_{\perp}^i) \cos \theta \sin \theta}{2k_f D_S^i \Delta T} \quad (17)$$

while for melting fronts ($V < 0$) we have:

$$V_m = - \frac{(D_{||}^i \sin^2 \theta + D_{\perp}^i \cos^2 \theta)G}{\Delta T} \frac{D_L^i + K D_S^i}{K D_S^i} \quad (18)$$

$$k_m = \left(\frac{(D_{||}^i \sin^2 \theta + D_{\perp}^i \cos^2 \theta)(D_S^i + D_L^i)G^2}{(D_S^i)^2 4K d_0 T_0 \Delta T} \right)^{1/3} \quad (19)$$

$$V_{dm} = - \frac{G(D_L^i + K D_S^i)(D_{||}^i - D_{\perp}^i) \cos \theta \sin \theta}{\Delta T K D_S^i} \quad (20)$$

Formulas (15–20) have been obtained by further assuming that:

$$3 \left(\frac{K}{4} \right)^{2/3} \left(\frac{d_0 T_0}{\Delta T} \right)^{1/3} \left(\frac{D_L^i + D_S^i}{D_L^i} \right)^{2/3} \frac{1}{(D_L^i + K D_S^i)^{1/3}} V_f^{1/3} \ll 1 \text{ in freezing} \quad (21a)$$

and

$$\frac{3}{4^{2/3}} \left(\frac{d_0 T_0 D_{22}^i (D_L^i + D_S^i)^2}{K \Delta T (D_L^i + K D_S^i)} \right)^{1/3} \frac{V_m^{1/3}}{D_S^i} \ll 1 \text{ in melting} \quad (21b)$$

We shall see later that these two inequalities are satisfied experimentally.

Let us emphasize at this stage that

$$\frac{V_{df}}{V_{dm}} \approx \frac{V}{Dk} \ll 1 \quad (22)$$

provided that inequalities (12) are satisfied.

Similar equations can be obtained when the hexagonal phase is anchored homeotropically (*i.e.* with the columns perpendicular to the glass plates) by replacing $D_{||}^i$ and D_S^i by $D_{\perp}^i$ in previous formulas. In this particular case, there is no cellular drift and we have:

$$V_f = \frac{(D_L^i + K D_{\perp}^i)G}{\Delta T} \quad (23)$$

$$k_f = \left(\frac{K(D_L^i + D_{\perp}^i)G^2}{4\Delta T D_L^i d_0 T_0} \right)^{1/3} \quad (24)$$

$$V_m = - \frac{G}{\Delta T} \frac{D_L^i + K D_{\perp}^i}{K} \quad (25)$$

$$k_m = \left(\frac{(D_{\perp}^i + D_L^i)G^2}{4D_{\perp}^i K d_0 T_0 \Delta T} \right)^{1/3} \quad (26)$$

Finally, we mention that we have intentionally neglected the attachment kinetics. We know from a previous work of Coriell and Sekerka [19] that this effect does not change the critical velocity (decreasing only the growth rate of the instability) but leads to an additional drift of the cells which can be written in the form (in freezing):

$$V_{d,kin} = - \frac{(\delta T_{kin,f})^2}{G\lambda_f} \frac{\partial \mu}{\partial \theta} \quad (27)$$

where $\delta T_{kin,f}$ is the kinetic temperature shift at V_f and $\lambda_f = 2\pi/k_f$ the critical wavelength. We shall see later that this contribution is completely negligible in our experiment.

In the following subsection, we give our main experimental results.

4.2. EXPERIMENTAL RESULTS. — Let us first discuss the experimental procedure.

We used 75 μm -thick samples in planar or homeotropic anchoring. The former are much easier to make than the latter because the columns spontaneously anchor parallel to the glass plates. Large monodomains of a few mm^2 are obtained in directional solidification by slowly growing the hexagonal phase in the temperature gradient. The sample is then rotated to orient the striations at an angle θ with respect to the temperature gradient.

In order to measure the critical velocity at freezing fronts, we increase very slowly the pulling velocity by small increments (typically 0.1 $\mu\text{m/s}$). At each increment, we wait for a time of the order of 2 or 3 times D^i/KV^2 which is the minimum time which is necessary to reach a quasi-stationary regime. In this way, we obtain a first critical velocity V^+ . In Figure 7, we show the cells at V^+ for freezing fronts in planar and homeotropic anchorings. We observe that the cells are not perfectly sinusoidal with a non-zero amplitude. We then decrease slowly the velocity till the front restabilizes. This occurs below a critical velocity V^- which is about 5 to 10% smaller than V^+ in our system. Let A be the amplitude of the cellular pattern. In Figure 8 we plotted A as a function of velocity V for a typical freezing front in planar orientation. The amplitude jump at V^+ as well as the small hysteresis $V^+ - V^-$ show that the cellular bifurcation is slightly subcritical in freezing.

We did the same measurements in melting, but did not observe any measurable hysteresis. This means that the bifurcation is supercritical within our experimental errors in melting. This result is compatible with the sinusoidal shape of the undulations at the onset in melting (see Fig. 9).

These results for melting are coherent with previous theoretical predictions concerning the nature of the bifurcation. Indeed, we know from a weakly nonlinear analysis that the bifurcation must be supercritical when K is close to 1 [20,21] or $D_S^i \approx D_L^i$ [22]. The fact that the bifurcation is weakly subcritical for freezing fronts is perhaps due to the presence of a meniscus which we know to make an angle of about 70° with the glass plates.

In the following, we shall consider that $V_f \approx V^+$ and we will neglect meniscus effects. This result is justified insofar as the bifurcation is weakly subcritical and we did not observe any significant variation of V^+ with the sample thickness (which we change from 50 to 150 μm).

Critical velocities and wavelengths are given in Figures 10a-b for freezing fronts in homeotropic anchoring, in Figures 11a-b for freezing front in planar orientation at $\theta = 0$ and in Figures 12a-b for melting fronts in the same orientation. Influence of the tilt angle θ is described in Figures 13a-c for freezing fronts and in Figures 14a-c for melting fronts.

The problem is now to fit these curves (12 in all) to the theoretical laws given in the preceding subsection.

4.3. DETERMINATION OF THE DIFFUSION COEFFICIENTS. — In order to determine the three diffusion coefficients D_L^i , $D_{||}^i$ and $D_{\perp}^i$, we have chosen to only fit the curves of critical and

(a)

(b)

Fig. 7. — a) Cellular patterns observed at the onset of instability in a planar sample ($\Delta T = 0.33$ °C, $V = 0.45$ $\mu\text{m/s}$, $G = 40$ °C/cm, freezing front); b) Idem in a homeotropic sample ($\Delta T = 0.26$ °C, $V = 0.534$ $\mu\text{m/s}$, $G = 40$ °C/cm, freezing front). Meniscus effects are clearly visible in these photographs.

of drift velocities. Indeed, we know from previous studies (for a review see [23]) that critical velocities are much less sensitive than wavelengths to the nature of the bifurcation. In this respect, a systematic analysis of experimental data in metallic alloys has shown that the critical wavelengths predicted by the linear theory are correct to within experimental error when the bifurcation is supercritical, whereas they are wrong by a factor of 2 (or more) when it is subcritical.

Fig. 8. — Cell amplitude A versus pulling velocity V during freezing of a planar sample ($\Delta T = 0.41^\circ\text{C}$, $G = 40^\circ\text{C/cm}$, $d = 75\ \mu\text{m}$).

In Figures 10-14 we plotted (curves in solid line) the theoretical predictions calculated from formulas (15-20, 23-26) by taking

$$\begin{aligned} D_L^i &= 3.2 \times 10^{-11}\ \text{m}^2/\text{s} \\ D_{||}^i &= 2.7 \times 10^{-11}\ \text{m}^2/\text{s} \\ D_{\perp}^i &= 1.8 \times 10^{-12}\ \text{m}^2/\text{s} \end{aligned} \quad (28)$$

which gives $D_{||}^i/D_{\perp}^i \approx 15$. We see that there is very good agreement between the linear theory and the experimental results as long as the critical and the drift velocities are concerned. The wavelength is also correctly predicted at melting fronts for which we found the bifurcation is supercritical. By contrast, the experimental wavelength is found to be 1.5 to 2 times smaller than the wavelength predicted by the linear theory at freezing fronts, which is expected for a weakly subcritical bifurcation.

To conclude this section, let us discuss the validity of the approximations made.

We must first verify that the wavelength is always smaller than the diffusion length in both phases. This assumption is the more severely tested for freezing fronts, for which we must check that

$$k_f \gg \frac{V_f}{2D_L^i} \quad \text{and} \quad k_f \gg \frac{V_f}{2D_S^i}, \quad \text{with} \quad V_f = (D_L^i + KD_S^i) \frac{G}{\Delta T} \quad (29)$$

With the preceding values of the diffusion coefficients and by taking $G = 40^\circ\text{C/cm}$ and $\Delta T = 0.3^\circ\text{C}$ we find $\frac{V_f}{2D_L^i} = 78\ \text{cm}^{-1}$ and $\frac{V_f}{2D_S^i} = 350\ \text{cm}^{-1}$ while we measure $k_f \approx 1000\ \text{cm}^{-1}$. Inequalities (29) are thus fulfilled.

We must also verify that capillary corrections are negligible. This is true if inequalities (21a,b) are both verified. In order of magnitude, they can be rewritten in the simplified form

$$\left(\frac{d_0 T_0}{\Delta T} \frac{V}{D^i} \right)^{1/3} \ll 1 \quad (30)$$

Fig. 9. — Cellular pattern at a melting front in a planar sample. This sequence of photographs have been taken at regular time intervals (4 mn) and show the drift of the cells. In this example, V_d is positive according to our notations ($\Delta T = 0.27$ °C, $G = 40$ °C/cm, $V = -0.45$ $\mu\text{m/s}$, $\theta = 18^\circ$).

With typical values, $d_0 = 1$ Å, $T_0 = 300$ K, $\Delta T = 0.3$ K, $V/D^i = 100$ cm^{-1} , we find $\left(\frac{d_0 T_0}{\Delta T} \frac{V}{D^i}\right)^{1/3} \approx 0.1$, so that inequality (30) is also satisfied in practice.

To better assess the validity of our approximations, we again calculated D_L^i from the experimental values of the critical velocity which we obtained at freezing fronts in homeotropic anchoring (Fig. 10a). These calculations were done numerically using Mathematica from the full dispersion relation by assuming that $D_S^i = 7 \times 10^{-8}$ cm^2/s . More precisely, we calculated

Fig. 10. — Critical velocity V_f (a) and cell wavelength λ_f (b) as a function of the temperature gradient G (impure sample at the azeotropic concentration, homeotropic anchoring, $\Delta T = 0.26$ °C).

D_L^i and k_f for each couple (G, V_f) by solving the two equations $\sigma_R = 0$ and $d\sigma_R/dk = 0$. The mean value of D_L^i we found in this way is 20% smaller than the value we have given previously. This difference is not really significant insofar as it is of the same order of magnitude as the experimental errors.

Finally, let us verify that the kinetics are negligible. The good agreement between the experimental results and the linear theory in which only the diffusion anisotropy is taken into account suggests it is true. In order to better convince ourselves, let us calculate the drift velocity given by equation (27) at the onset of instability. By taking $G = 40$ °C/cm,

Fig. 11. — Critical velocity V_f versus $G/\Delta T$ (a) and cell wavelength λ_f versus G (b) (impure sample at the azeotropic concentration, planar anchoring, $\theta = 0$, $\Delta T = 0.33^\circ\text{C}$ in (b)).

$\partial\mu/\partial\theta \approx 0.2\mu$, $\mu = 210 \mu\text{m/s/}^\circ\text{C}$, $\Delta T = 0.33^\circ\text{C}$, $V_f = 0.45 \mu\text{m/s}$, $\lambda_f = 75 \mu\text{m}$, we find:

$$V_{d,\text{kin}} = -\frac{(\delta T_{\text{kin},f})^2}{G\lambda_f} \frac{\partial\mu}{\partial\theta} \approx -6.4 \times 10^{-4} \mu\text{m/s}$$

As expected, this value is much smaller than the drift velocity measured experimentally at freezing ($V_{\text{df}} \approx 7 \times 10^{-2} \mu\text{m/s}$) or melting fronts ($V_{\text{dm}} \approx 1 \mu\text{m/s}$).

In conclusion, we estimate that our diffusion coefficients are known to within $\pm 30\%$.

In the following section, we analyze the front instability in pure quasi-azeotropic mixtures.

Fig. 12. — Critical velocity V_m (a) and cell wavelength λ_m (b) as a function of G (impure sample at the azeotropic concentration, planar anchoring, $\theta = 0$, $\Delta T = 0.33$ °C in (b)).

5. Mullins-Sekerka Instability in a Pure Quasi-Azeotropic Mixture

We performed similar experiments at freezing and melting fronts in planar samples. Whereas we observed the cellular instability at freezing fronts, we were not able to see it during melting because of the nucleation ahead of the interface.

Let us emphasize at first that the problem is a bit different from that of dilute systems because the liquidus and the solidus lines are not straight lines but are replaced by two parabolas (see Eq. (1)). The Gibbs-Thomson relation and the partition law for the concentration at the curved front are also modified. Let $C_{L,S}$ be the local concentrations of $C_{12}EO_6$, $u_{L,S} = C_{L,S} - C_0$ the

Fig. 13. — Critical velocity V_f (a), cell wavelength λ_f (b) and drift velocity V_{df} (c) as a function of angle θ (impure sample at the azeotropic concentration, planar anchoring, $G = 40^\circ\text{C}/\text{cm}$).

concentration shifts from the azeotropic concentration, and C_∞ the average concentration in the sample. The liquidus temperature is then

$$T_L = T_0 + \alpha_L u_L^2 - d_0 T_0 \kappa, \quad (31)$$

where κ is the local curvature of the front while the concentration shift is

$$u_S = K' u_L - \frac{d_0^c u_\infty \kappa}{K'} \quad (32)$$

In this formula, d_0^c is a chemical capillary length of the order of $0.05d_0$ (for an estimate see [12]).

Fig. 13. — (Continued.)

Before determining the mass diffusion coefficients D_L , $D_{||}$ and $D_{\perp}$ in the micellar and hexagonal phases, we shall first generalize the calculations of Misbah [12] for quasi-azeotropes by taking into account the diffusion anisotropy in the solid phase. Then, we shall see how to calculate the nucleation threshold at melting fronts. Finally, we shall give the experimental results and the values of the three diffusion coefficients.

5.1. CRITICAL VELOCITY AND CELLULAR DRIFT AT FREEZING FRONTS IN QUASI-AZEOTROPES. — Let σ be the complex growth rate of a sinusoidal deformation of wavevector k . A linear-stability analysis gives the dispersion relation

$$\sigma u_{\infty}^2 4\alpha_L \frac{1-K'}{K'^2} = \left(\sqrt{V^2 + 4D_L^2 k^2} + 4D_L \sigma - V \right) \left(G + d_0 T_0 k^2 - 2\alpha_L u_{\infty}^2 \frac{V(K'-1)}{K'^2 D_L} \right) + K' \left(V + \sqrt{4D_S^2 k^2 + V^2 + 4D_{12}^2 k V + 4D_{22}^2 \sigma} \right) \left(G + d_0 T_0 k^2 - \frac{d_0^c u_{\infty}^2 2\alpha_L k^2}{K'^3} \right) \quad (33)$$

By assuming that

$$k \gg \frac{V}{2D_L} \quad \text{and} \quad k \gg \frac{V}{2D_S},$$

we can easily separate the real and imaginary parts:

$$2\alpha_L u_{\infty}^2 \frac{(1-K')}{K'^2} \sigma_I = K' \left(G + d_0 T_0 k^2 - d_0^c \frac{2u_{\infty}^2 \alpha_L}{K'^3} \frac{D_{12} V}{2D_S} \right) \quad (34)$$

$$2\alpha_L u_{\infty}^2 \frac{(1-K')}{K'^2} \sigma_R = \quad (35)$$

$$GV \frac{(1-K')}{2} - \frac{\alpha_L u_{\infty}^2 (K'-1) V^2}{K'^2 D_L} - k \left[G(D_L + K' D_S) - 2\alpha_L u_{\infty}^2 V \frac{(K'-1)}{K'^2} \right] + k^2 \left[d_0 T_0 V \frac{(1-K')}{2} + \frac{d_0^c \alpha_L u_{\infty}^2 V}{K'^2} - k^3 \left(d_0 T_0 (D_L + K' D_S) - \frac{d_0^c \alpha_L u_{\infty}^2 2D_S}{K'^2} \right) \right]$$

Fig. 14. — Critical velocity V_m (a), cell wavelength λ_m (b) and drift velocity V_{dm} (c) as a function of angle θ (impure sample at the azeotropic concentration, planar anchoring, $G = 40^\circ\text{C/cm}$).

By using the instability criteria (11) and by neglecting the capillary lengths, we obtain the following expression for the critical velocity:

$$V_f = \frac{GK'^2(D_L + K'D_S)}{2\alpha_L u_\infty^2(K' - 1)} \quad (36a)$$

or, equivalently:

$$V_f = \frac{(1 + K')}{2} \frac{(D_L + K'D_S)G}{\Delta T} \quad (36b)$$

Fig. 14. — (Continued.)

Here the freezing range is given by

$$\Delta T = \alpha_L u_{\infty}^2 (K' - 1) \frac{(1 + K')}{K'^2} \quad (37)$$

The critical wavevector and the drift velocity are given by

$$k_f = \left(\frac{\alpha_L (K' - 1) u_{\infty}^2 (D_L + D_S) V_f^2}{2K' d_0 T_0 D_L (D_L + K' D_S)^2} \right)^{1/3} = \left(\frac{K' (1 + K') (D_L + D_S) G^2}{8d_0 T_0 D_L \Delta T} \right)^{1/3} \quad (38)$$

and

$$V_{df} = \frac{K' (1 + K') G V_f (D_{||} - D_{\perp}) \cos \theta \sin \theta}{4 \Delta T D_S k_f} \quad (39)$$

Let us emphasize that V_f and k_f do not depend on the sign of u_{∞} which means that, within the approximations (d_0^c negligible), there is no asymmetry with respect to the azeotropic point.

We do not generalize these results for melting because we never observed the Mullins-Sekerka instability in this case. On the other hand, we observed that nucleation systematically occurs (Fig. 15) above some critical velocity which we calculate in the following subsection.

5.2. CONSTITUTIONAL SUPERHEATING AT MELTING FRONTS. — Nucleation may occur when regions of constitutional superheating are present ahead of the interface. This condition is fulfilled when the concentration profile, of equation (with $V < 0$):

$$u_L = u_{\infty} \quad (T > T_i) \quad (40a)$$

$$u_S = u_{\infty} \left[1 + (K' - 1) \exp \left(-\frac{V(T - T_i)}{G D_{22}} \right) \right] \quad (T < T_i) \quad (40b)$$

penetrates into the region of coexistence of the two phases (Fig. 16). The interface temperature

Fig. 15. — Nucleation ahead of the interface during melting (pure quasi-azeotropic mixture, $\Delta T = 0.45^\circ\text{C}$, $G = 40^\circ\text{C/cm}$, $\theta \approx 40^\circ$, $V = V_{\text{nucl}} = -2.9 \mu\text{m/s}$).

Fig. 16. — Graphic determination of the "constitutional superheating" velocity V_{CS} . This velocity is reached when the concentration profile is just tangent to the solidus line. The concentration C_{Si} at the interface is equal to $C_0 + K'u_\infty$.

T_i is given by $T_i = T_0 + \alpha_L u_\infty^2$. By requiring that the concentration profile be tangent to the liquidus line, we obtain the velocity of constitutional superheating:

$$V_{\text{CS}} = -\frac{D_{22}G}{2K'(K' - 1)\alpha_S u_\infty^2} = -\frac{(D_{\parallel} \sin^2 \theta + D_{\perp} \cos^2 \theta)G(1 + K')}{2K'\Delta T} < 0 \quad (41)$$

As a matter of fact, the hexagonal phase can be superheated by a certain amount $\delta T_{\text{nucl}} = T_{\text{nucl}} - T_S \approx 0.08^\circ\text{C}$ which we found independent of the freezing range (see Sect. 1). Thus, nucleation occurs in practice at a velocity $V_{\text{nucl}} < V_{\text{CS}}$. At this velocity, the concentration profile is tangent to the shifted line $T_S + \delta T_{\text{nucl}}$. This condition being difficult to express analytically, we preferred a graphic method to find V_{nucl} . This procedure gives a formula which is similar to (41) in which ΔT must be corrected by a dimensionless function $\text{cor}(\Delta T)$

Fig. 17. — Graphic determination of velocities V_{CS} and V_{nucl} . The latter is reached when the concentration profile becomes tangent to the nucleation line $T_S + \delta T_{nucl}$. For each ΔT , we calculated in this way the ratio $cor(\Delta T) = V_{CS}/V_{nucl}$.

Fig. 18. — Function $cor(\Delta T)$ graphically determined.

which can be determined graphically (Fig. 17):

$$V_{nucl} = - \frac{(D_{||} \sin^2 \theta + D_{\perp} \cos^2 \theta) G(1 + K')}{2K' \Delta T cor(\Delta T)} \quad (42)$$

Fig. 19. — Critical velocity V_f (a) and cell wavelength λ_f (b) as a function of the temperature gradient G (pure quasi-azeotropic mixture, planar sample, $\theta = 0$). The superscript + (resp. -) indicates that $C_{C_{12}EO_6} > C_0$ (resp. $< C_0$). In (b) $\Delta T^+ = 0.59^\circ C$.

The function $\text{cor}(\Delta T)$ is plotted in Figure 18. We see that this correction is important and changes V_{nucl} by a factor 2 to 3 in the range of the ΔT chosen.

We have now all the theoretical tools to calculate the diffusion coefficients from the experimental results. The latter are given in the following subsection.

5.3. EXPERIMENTAL RESULTS FOR PURE QUASI-AZEOTROPES. — We measured the critical velocity V_f and the wavevector k_f of freezing fronts in planar samples when $\theta = 0$. These results are reported in Figures 19a-b as a function of the freezing range ΔT . Our measurements were done on both sides of the azeotropic point. We saw no difference between measurements done

Fig. 20. — Nucleation velocity V_{nucl} in melting *versus* G at $\theta = 0$ (a) and *versus* θ at $G = 40$ °C/cm (b) (pure quasi-azeotropic mixture, planar sample).

at $+\Delta T$ and $-\Delta T$. This absence of asymmetry means that the chemical capillary length d_0^c indeed plays a negligible role, as expected from Misbah's calculations. Measurements at $\theta > 25^\circ$ were impossible because of the nucleation of solid germs ahead of the interface (note that the critical velocities are 5 to 10 times larger in this experiment than in the previous one with impurities).

At melting fronts, we measured the nucleation velocity for different ΔT as a function of the temperature gradient G (at $\theta = 0$, Fig. 20a) and of the angle θ (at fixed G , Fig. 20b). In these two graphs, we corrected ΔT by using the $\text{cor}(\Delta T)$ function given in Figure 18.

We are now in a position to calculate the diffusion coefficients.

5.4. MASS DIFFUSION COEFFICIENTS. — As before, we do not fit the wavelength curve to its theoretical expression (38) because the bifurcation is subcritical. On the other hand, the best fits of the experimental results depicted in Figures 19a and 20 to the theoretical laws (36b) and (42) (solid lines in these figures) give the three diffusion coefficients:

$$\begin{aligned} D_L &= 1.2 \times 10^{-10} \text{ m}^2/\text{s} \\ D_{||} &= 2.3 \times 10^{-10} \text{ m}^2/\text{s} \\ D_{\perp} &= 8.5 \times 10^{-11} \text{ m}^2/\text{s} \end{aligned}$$

In this case $D_{||}/D_{\perp} \approx 2.7$, which is markedly smaller than the values found for the impurities. We can now calculate the wavelength with formula (38). As expected, we find wavelengths about two times larger than the measured ones.

Finally, let us emphasize that the approximations made ($k \gg V/2D$ and negligible capillarity) are satisfied, except in samples for which $\Delta T < 0.2$ °C where $k \approx V/2D$. For this reason, we did not take into account the critical velocities measured in these samples when we fit the experimental data of Figure 19a.

6. Conclusion

We have observed the Mullins-Sekerka instability in a lyotropic system of a non-ionic surfactant $C_{12}EO_6$ at the hexagonal-micellar interface. We have measured the critical and the drift velocities at freezing and melting fronts, which allowed us to determine the diffusion coefficients and their anisotropy in the two phases, both for the impurity and the surfactant concentration field. Our results are summarized in Table I. We added, for comparison, the values of the individual diffusion coefficients of $C_{12}EO_6$ and of water measured by NMR. We did ourselves the measurements for $C_{12}EO_6$ (see the appendix) whereas the value given for the water in the micellar phase was found in the literature [31]. We emphasize the difficulty to precisely measure $D_{\perp}$ in the hexagonal phase because of its smallness with respect to $D_{||}$. For this reason, its value given in Table I is only approximate.

Table I.

D (m ² /s)	Impurity	$C_{12}EO_6$	H ₂ O	Collective
D_L	3.2×10^{-11}	1.7×10^{-11}	1.0×10^{-9}	1.2×10^{-10}
$D_{ }$	2.7×10^{-11}	7×10^{-11}		2.3×10^{-10}
$D_{\perp}$	1.8×10^{-12}	3×10^{-12}		8.5×10^{-11}

This table shows that the diffusion coefficients of the impurity and of the $C_{12}EO_6$ are of the same order of magnitude, which certainly means that these two species are chemically close to each other and of comparable size. This is compatible with the degradation scheme we have proposed in Section 2. We also emphasize that, as expected for amphiphilic molecules, diffusion perpendicular to the columns is much faster than parallel to them, by a factor of 15.

By contrast, the hydrodynamic diffusion coefficients of the concentration field are halfway between the diffusion coefficients of the $C_{12}EO_6$ and of the water. This perhaps explains why their anisotropy in the hexagonal phase is rather small ($D_{||}/D_{\perp} \approx 2.7$).

Finally, we measured the kinetic coefficient. We found the same value in freezing and in melting, which means that kinetics are linear and symmetrical. This value is of the same order of magnitude as in the C8HET, a hexaester of triphenylene in which we measured $\mu \approx 130$ $\mu\text{m/s/}^\circ\text{C}$ [15].

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Appendix

Measure of the $C_{12}EO_6$ Diffusion Coefficients by Pulsed Field Gradient NMR

To complement the analysis of directional growth experiments, it is interesting to compare the diffusion coefficients given above to those which may be measured independently by pulsed-field gradient NMR. With this technique, which has been widely used in surfactant/water systems [24, 25] self-diffusion coefficients of a given species are measured.

The standard proton pulsed field technique is used [26]. A spin echo is produced by a $90^\circ - 180^\circ$ radiofrequency pulse sequence. A field gradient is applied during a time δ , after each radiofrequency pulse. The gradient pulses are separated by a duration Δ . The diffusion coefficient is extracted from the ratio of the echo amplitudes A_G and A_0 , respectively with and without field gradients. In an isotropic phase, this ratio is given by:

$$\frac{A_G}{A_0} = \exp[-\gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \quad (A.1)$$

where γ is the proton magnetogyric ratio ($\gamma = 2.6753 \times 10^8 \text{ s}^{-1} \text{ T}^{-1}$), D the self-diffusion coefficient and G the gradient magnitude. The diffusion coefficient D may be determined by varying either the gradient magnitude or the duration δ . The distance over which diffusion is measured is typically of the order of $1 \mu\text{m}$. Therefore the above formula is valid if the diffusion is not limited to regions smaller than $1 \mu\text{m}$. The field gradient amplitude was calibrated precisely with pure water at room temperature ($D_0 = 2.036 \times 10^{-9} \text{ m}^2/\text{s}$ at 20°C [27]).

In an anisotropic phase, the situation is more complicated, especially when it is not possible to orient the phase at the magic angle macroscopically. First, the spin echo amplitude decays much faster, due to the presence of residual dipolar interactions. This makes it difficult to achieve long enough Δ durations. However, this drawback may be eventually compensated by using stronger gradient amplitudes, or by using the stimulated echo technique, in which the spin magnetization is stored as longitudinal component (undergoing a T_1 relaxation, *i.e.* a much slower decay) during a given delay [28]. On the other hand, the anisotropy in the diffusion itself has to be taken into account [29]. If oriented regions in the sample are supposed to be significantly larger than $1 \mu\text{m}$, the ratio of echo amplitudes in a microscopically isotropic powder sample may be written as

$$\frac{A_G}{A_0} = \frac{\int_0^\pi M_\theta(t) \exp[-\gamma^2 G^2 D(\theta) \delta^2 (\Delta - \delta/3)] \sin \theta d\theta}{\int_0^\pi M_\theta(t) \sin \theta d\theta} \quad (A.2)$$

Here, $D(\theta)$ is the effective diffusion coefficient in the direction of the field gradient:

$$D(\theta) = D_{||} \cos^2 \theta + D_{\perp} \sin^2 \theta \quad (A.3)$$

and $M_\theta(t)$ the (inhomogeneous) contribution to the decay related to residual dipolar interactions. By neglecting the angular variation in θ in the factor $M_\theta(t)$, equation (A.2) simplifies

Fig. 21. — Diffusion coefficient of the surfactant ($C_{12}EO_6$) in the micellar phase measured by NMR as a function of the temperature at the azeotropic concentration. The line is the best fit to an Arrhenius law.

and can be rewritten in the form

$$\frac{A_G}{A_0} = \frac{\sqrt{\pi}}{2} \frac{\exp(-\rho D_{\perp})}{\sqrt{\rho(D_{\parallel} - D_{\perp})}} \operatorname{erf}\left(\sqrt{\rho(D_{\parallel} - D_{\perp})}\right) \quad (\text{A.4})$$

with $\rho = G^2 \gamma^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)$ and $\operatorname{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t \exp(-x^2) dx$.

Experiments have been performed on a Bruker CXP 90 spectrometer equipped with a 2 T magnet and a home built pulsed field gradient probe head. The gradient magnitude varies from 0 to 3 T m⁻¹. The temperature is regulated to within 0.1 °C with a Bruker VT100 unit, the uncertainty in the absolute calibration of the temperature being of the order of 1 °C. The transition temperature is detected in the NMR experiment by a sharp narrowing of the signal.

The surfactant self-diffusion coefficient was measured in a sample prepared in deuterated water, as a function of temperature, in the micellar phase (above the transition), at a concentration $C = 49.6\%$ close to the azeotropic point. Here, diffusion coefficients are measured with an accuracy better than 5%. Due to possible exchange between deuterated water and OH groups of the surfactant, there may be a contribution from the water in the measured proton diffusion [30, 31]. This effect was shown in reference [30] to be less than 2% in the concentration range considered herein. There also may be a contribution from the exchange of surfactant molecules between micelles, leading to an effective measured diffusion coefficient D_{mes} expressed as:

$$D_{\text{mes}} = c \dot{D}_{\text{mic}} + (1 - c) D_{\text{mon}} \quad (\text{A.5})$$

where D_{mic} is the micelle diffusion coefficient, D_{mon} that of the isolated surfactant molecules, $1 - c$ the fraction of the molecules in solution, which is approximately equal to the critical micellar concentration (cmc). With $D_{\text{mes}} \approx 1.7 \times 10^{-11}$ m²/s close to (above) the transition, $1 - c \approx 6 \times 10^{-5}$ [32] and $D_{\text{mon}} \approx 4 \times 10^{-10}$ m²/s [30], it is clear that surfactant molecules in

Fig. 22. — $\ln(A_G/A_0)$ as a function of $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$. The solid lines correspond to the best fits to equation (A.2). a) $T = 308$ K; b) $T = 298$ K.

solution give only negligible contribution, and the micelle self-diffusion is effectively measured to an excellent approximation. From the slope measured in Figure 21, the activation energy for the micelle diffusion is $E_a = 39.6$ kJ/mol. However the micelles are probably not spherical in this system [11]. A possible change in the shape of the aggregates in rising the temperature has eventually to be taken into account as well in the temperature variation of the diffusion coefficient [33–35]. This problem is not discussed herein.

The self-diffusion coefficients of deuterated water were measured in reference [31] in the micellar phases of $C_{12}EO_5$ and $C_{12}EO_8$ samples. The diffusion coefficient of deuterated water depends on the fraction of water bounded to the poly(ethylene oxid) chains, and on an

obstruction factor which is to the order 0.7 to 0.8 depending on the shape of the aggregates [31]. The fraction of bound water does not exhibit a very strong temperature variation. It depends essentially on the molar ratio m_{D_2O}/m_{EO} relating the numbers of water molecules and of ethylene oxide groups. For a molar ratio of 3.75, as it is the case here, the fraction of bound water is of order 0.7 [31]. Thus the diffusion coefficient of deuterated water may be estimated to be of the order of $10^{-9} \text{ m}^2/\text{s}$ close to the transition.

In the hexagonal phase, the stimulated echo sequence was used. The diffusion curves obtained when plotting $\ln(A_G/A_0)$ as a function of $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ are not linear, due to the diffusion anisotropy (Fig. 22). The curve measured close to (below) the transition is reported in Figure 22a while the curve measured 10 °C below the transition (298 K) is given in Figure 22b. Both curves were fit to equation (A.2), in which we neglect the angular variation in the dipolar line shape, *i.e.* in the factor $M_\theta(t)$. These fits give the two diffusion coefficients $D_{||}$ and $D_{\perp}$ and confirms that $D_{\perp}$ is much smaller than $D_{||}$. More precisely, we found:

$$\begin{aligned} D_{||} &= 7 \pm 1.5 \times 10^{-11} \text{ m}^2\text{s}^{-1}, & D_{\perp} &= 3 \pm 2 \times 10^{-12} \text{ m}^2\text{s}^{-1} & \text{at } T = 308 \text{ K} \\ D_{||} &= 2.4 \pm 0.6 \times 10^{-10} \text{ m}^2\text{s}^{-1}, & D_{\perp} &\ll D_{||} \text{ (not measurable)} & \text{at } T = 298 \text{ K} \end{aligned}$$

Although the measurement of $D_{\perp}$ is very imprecise, it is clear that the diffusion anisotropy in the hexagonal phase increases on lowering the temperature, and that parallel diffusion is much faster at low temperature than near the transition to the micellar phase. This is probably related to the appearance of defects along the cylinders when the transition is approached. This effect is left for future investigations.

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