J. Phys.: Condens. Matter **2** (1990) 5907–5912. Printed in the UK

LETTER TO THE EDITOR

A self-diffusion study of polymer-like micelles

A Ott†, W Urbach†, D Langevin†, P Schurtenberger‡, R Scartazzini‡ and P L Luisi‡

† Laboratoire de Physique Statistique, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cédex 05, France

‡ Institut für Polymere, ETH Zentrum, Zürich, Switzerland

Received 4 May 1990

Abstract. We present a self-diffusion study of long cylindrical reverse micelles of lecithin in an organic solvent. The results are compared with those obtained for similar micelles of CTAB (cethyltrimethylammonium bromide) in brine. Qualitatively we observe a similar behaviour for both systems. The measured self-diffusion coefficient D_s has a power law dependence on the surfactant concentration. However, the exponent, which is salinity-dependent in the CTAB system, is constant and in good agreement with a theory for living polymers in the lecithin system. In the case of very elongated lecithin and CTAB micelles, D_s becomes independent of surfactant concentration.

Considerable theoretical and experimental interest has recently been devoted to 'living polymers', i.e. flexible linear macromolecules that can break and recombine [1–4]. Examples of such systems are end-functionalised polymers, plastic sulphur or, as in this paper, worm-like micelles. Micelles are aggregates of amphiphilic molecules in a solvent (water or oil). The aggregation of these molecules is spontaneous above a well-defined concentration called the critical micellar concentration. The shapes of these aggregates may differ (spheres, rods, disks) depending upon various parameters such as the nature of the amphiphilic molecules, their concentration, the presence and the nature of added salt, the temperature, etc.

The analogy between worm-like micelles and polymer solutions has been suggested [5] and demonstrated experimentally [6, 7]. Above a cross-over concentration c^*, these micelles entangle and form a transient network similar to that found in semidilute polymer solutions. However, the dynamical behaviour of these systems is different from that of ordinary polymer solutions or melts because the chains can break and recombine reversibly. We have previously performed self-diffusion measurements on cylindrical micelles made of CTAB (cethyltrimethylammoniumbromide) in potassium bromide aqueous solutions [8]. The data were consistent with the transient character of the aggregates. The self-diffusion coefficient was found to have a power law dependence on surfactant concentration, as for entangled polymers solutions, but the exponent depends on salt concentration. This variation was attributed to an increase of the ionic strength with surfactant concentration which modifies the growth law of the micelles [9].

In this article we present similar measurements on cylindrical reverse micelles of soybean lecithin in the organic solvent isooctane, where ions are insoluble and will not affect

0952-8984/90/265907 + 06 $03.50

the growth law. In this system, the viscosity of the reverse micellar solutions was found to increase dramatically upon the addition of very small quantities of water [10]. It was then postulated that the addition of water to lecithin/isooctane solutions induces one-dimensional micellar growth into long cylindrical reverse micelles. This structural model was subsequently tested by means of small-angle neutron scattering (SANS), quasielastic light scattering (QELS), and rheological measurements [11, 12]. Strong evidence for the presence of long and cylindrical reverse micellar aggregates and the formation of a transient network above c^* was found. The substantial increase of the micellar contour length L with increasing water-to-lecithin molar ratio (w_0) was directly observed using SANS from shear-aligned micellar solutions [13]. Here we present a systematic study of the dependence of the self-diffusion coefficient D_s on both lecithin concentrations and w_0. The results are compared with those from CTAB solutions at high salt concentration, where the ionic strength remains approximately constant when the surfactant concentration is varied.

We now briefly recall the main predictions for the self-diffusion of living polymers. Following the reptation theory, the self-diffusion coefficient D_s of entangled polymers depends on the number of monomers per chain N and on the monomer concentration c [14]:

$$D_s \sim N^{-2} c^{-1.75}. \tag{1}$$

In micellar systems, the chain length is not constant and varies with concentration. Based on a multiple-chemical-equilibrium analysis, Mukerjee [15] has proposed a dependence of the weight average aggregation number of

$$N \sim c^{\alpha} \tag{2}$$

with $\alpha = \frac{1}{2}$, assuming no interaction between micelles. The same growth law has been proposed by Safran *et al* [16] and Blankschtein *et al* [17]. However, there are also suggestions that the exponent could be higher: scaling arguments led Cates to $\alpha = 0.6$ [2]; Gelbart *et al* found $\alpha = 1$ by extending the Mukerjee model to higher concentrations taking into account excluded volume interactions [18]. Combining these models with (1) leads to

$$D_s \sim c^{x} \tag{3}$$

with $-3.75 \leqslant x \leqslant -2.75$.

Giant cylindrical micelles can break and recombine, and this affects the self-diffusion process. A theoretical approach has been proposed recently by Cates [2] who described the dynamics properties by introducing two characteristic time scales:

(i) t_R—the classical reptation time for a chain of length N;
(ii) t_B—the mean time for the chain to break into two pieces.

If $t_R < t_B$ stress relaxation is due to reptation; if $t_R > t_B$ it can be characterised by a new intermediate time scale: $t = (t_B t_R)^{1/2}$. The mean-field version of the model leads to $\alpha = \frac{1}{2}$ and in the regime $t_R > t_B$, $x = -\frac{5}{3}$.

We will now describe the materials and methods used.

Reverse micellar solutions of lecithin in isooctane were prepared as described in [12], and studied at a temperature of 25 °C.

The long-time self-diffusion coefficient was measured by tracer diffusion using the technique of fluorescence recovery after fringe-pattern photobleaching (FRAP). A small quantity of water-soluble fluorescent dye was added to the solutions (10^{-4}–10^{-5} M l^{-1}).

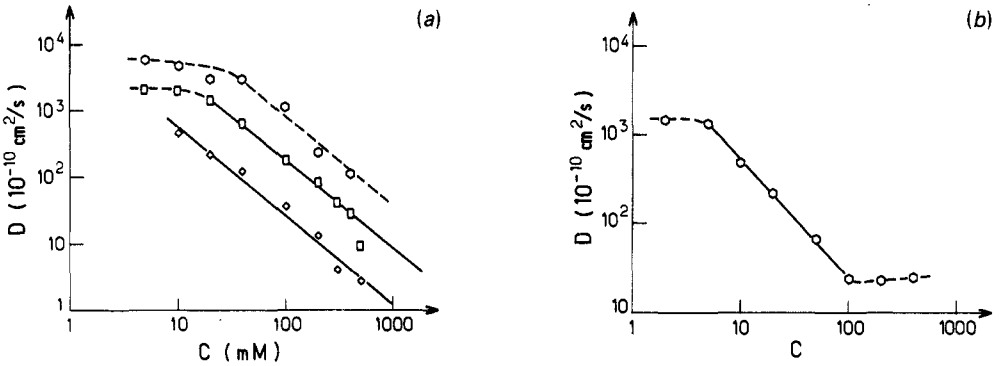

Figure 1. (*a*) Log–log plot of self-diffusion coefficient D_s versus lecithin concentration in isooctane solutions at 25 °C: ○, $w_0 = 0$; □, $w_0 = 1$; ◇, $w_0 = 2$. The full curves are least-squares fits; the broken curves are guides for the eye. The slopes for the full curves are −1.32 for $w_0 = 1$ and −1.35 for $w_0 = 2$. (*b*) CTAB + 0.5 M KBr at 35 °C. The full curve is a least-squares fit. Its slope is −1.32.

When strongly illuminated, the fluorescence is irreversibly destroyed. The relaxation of the non-uniform fluorescence distribution is detected by a low-intensity beam and D_s can be calculated from the recovery time τ: $D_s = 1/\tau q^2$, where $q = 2\pi/i$, i being the fringe spacing.

In the set-up, the fringe pattern is modulated to improve the signal-to-noise ratio. Experiments were made at at least three different i-values to verify that D_s is proportional to i^2. For further details see [19–21].

To check if the dye remains attached to the micelle, we performed measurements with hexadecanoylaminofluorescein, dodecanoylamino fluorescein and pure fluorescein. No difference between the diffusion coefficients was observed although the fractions of time spent by these dyes in the solvent are very different [8]. We have also checked the influence of dye concentration that was varied by one order of magnitude: this did not affect the diffusion coefficients either. We finally checked whether there was any bleaching due to the low-intensity beam during the recovery phase: we lowered the beam intensity by approximately one to two orders of magnitude, but no changes were measurable within the experimental accuracy.

We now present our results.

Our experimental data are summarised in figures 1 and 2, where we have plotted the values of D_s versus surfactant concentration on a log–log scale. In figure 1 the experimental errors correspond approximately to the size of the points.

Figure 1(*a*) shows the data for $w_0 = 0$, 1 and 2. After a cross-over from a dilute regime into a semidilute regime, D_s exhibits a power law dependence on surfactant concentration. The measured recovery curves are different in the two regimes: slightly non-exponential in the dilute regime, and single exponential in the semi-dilute regime (see figure 3). The overlap threshold c^* decreases with increasing w_0.

A completely different behaviour is observed at higher values of w_0 (figure 2). Here, D_s is either independent of concentration ($w_0 = 2.5, 4.0$) or increases with concentration ($w_0 = 3.0$). The solutions with $w_0 = 2.5$ show in addition a 'hyperdiffusion' at low lecithin concentration; diffusion is accelerated, i.e. $t^\beta = \langle r^2 \rangle$ with $\beta > 1$. The exponent a decreases with increasing concentration from $\beta = 1.5$ at $c = 40$ mM to $\beta = 1.0$ at $c =$

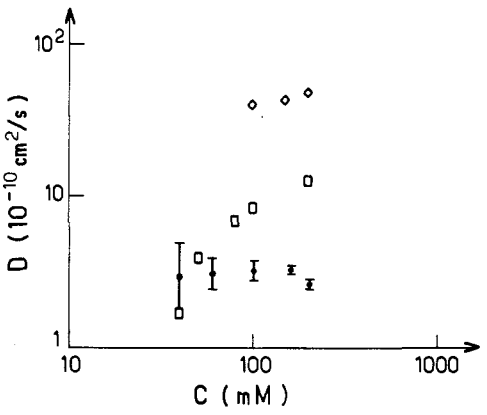

Figure 2. D_s versus lecithin concentration at 25 °C: ●, $w_0 = 2.5$; □, $w_0 = 3$; ◇, $w_0 = 4$.

200 mM. Similar observations were made for the CTAB system at very large salt concentrations. The explanation of this unusual behaviour will be discussed elsewhere [22].

As shown in figure 1(*a*), D_s decreases with increasing w_0 for lecithin reverse micellar solutions. This is in agreement with the previously postulated water-induced one-dimensional growth of lecithin reverse micelles [11]. The observed decrease of c^* with increasing w_0 is also consistent with an increase of the micellar length with increasing water content. A similar trend has already been observed with QELS experiments [11].

For $w_0 \leqslant 2.0$ and for CTAB at high salt content (figure 1(*b*)), we have measured an exponent $x = 1.35 \pm 0.05$ for the dependence of the self-diffusion coefficient on concentration. The exponent is remarkably independent of the specific surfactant or solvent. Its value differs significantly from the prediction for classical polymer behaviour, but agrees quite well with the living polymer model developed by Cates in the limit $t_R > t_B$ [2]. This model is further supported by the change in shape of the fluorescence recovery curves from the dilute to the semidilute regime where it becomes exponential (figure 3). (In the dilute regime, the micellar solution is made of polydisperse amphiphile aggregates; the resulting recovery curve is a superposition of the curves due to each species, and is not exponential.)

A different behaviour can be observed for $w_0 \geqslant 2.5$. Under these conditions the micelles have a very large contour length, and the viscosity reaches a maximum (at $w_0 = 3.0$) [11, 12]. This leads to very slow reptation times t_R. Other mechanisms for probe diffusion could then dominate, like the breathing modes of the polymer-like chain in its tube and the Rouse-like motion of stretches of chains shorter than the entanglement length [1]. A similar behaviour with a concentration-independent value of D_s can be observed for CTAB for $c \geqslant 100$ mM (see figure 2(*b*)). It is interesting to note that for lecithin/isooctane reverse micelles at $w_0 = 2.5$ and 3.0, a power law dependence for the zero-shear viscosity on concentration has been reported with an exponent that is significantly below the predictions for both the classical polymer behaviour as well as the living polymer model [11, 12].

For $w_0 = 4.0$, the values of D_s have now increased by almost an order of magnitude. This increase in D_s coincides with a decrease of the zero-shear viscosity [11, 12]. However, additional experimental investigations will be required in order to distinguish unambiguously between a decrease of the average micellar size and a change in the micellar kinetics (i.e. a decrease of the micellar lifetime), which would both result in such a combined increase of D_s and decrease of the viscosity.

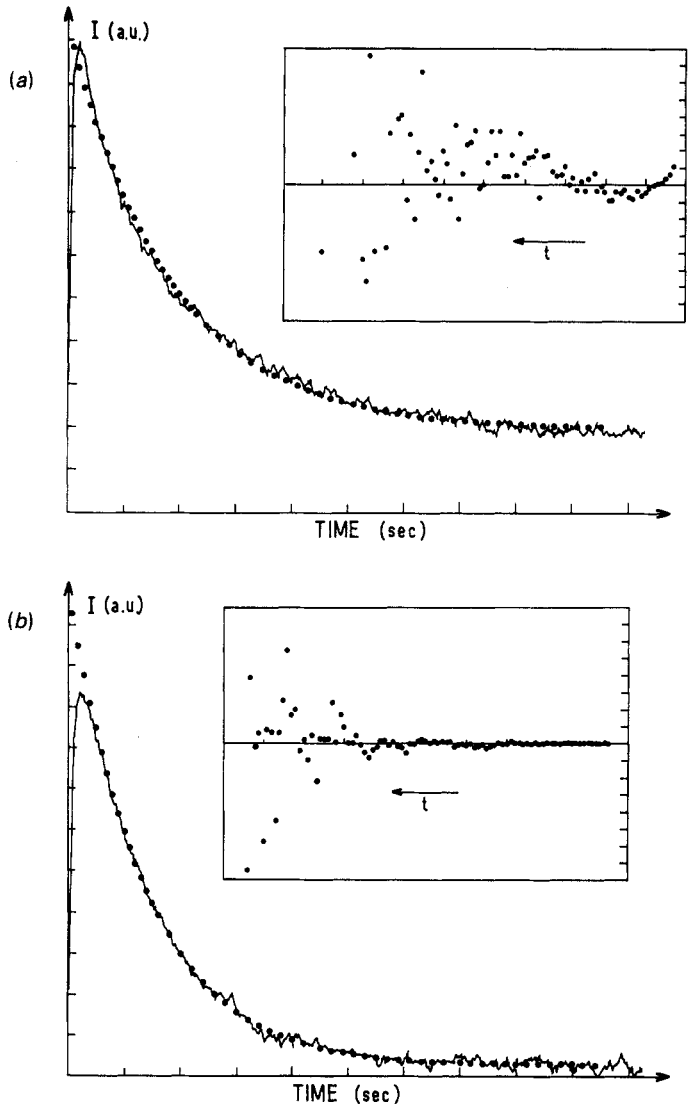

Figure 3. Typical decrease of the modulated fluorescence intensity (in arbitrary units) versus time. The curve is the experimental curve (the initial section where the signal increases with time is due to the finite response time of the lock-in amplifier). The dots represent the exponential fit. (*a*) Dilute sample. (*b*) Semidilute sample. Insets: plots of the residues (difference between experimental and theoretical curves). It is clear that the curve in (*a*) is non-exponential whereas the curve in (*b*) is exponential.

In conclusion the self-diffusion coefficient of long cylindrical micelles has a power law dependence on concentration, as for entangled polymers solutions. The exponent, close to -1.35, is remarkably independent of the micellar system, provided that, in the case of ionic surfactants, the ionic strength does not vary with concentration. The exponent differs from that predicted from polymer theories, but is close to the prediction of the Cates model for 'living polymers'. In a regime where diffusion is caused by two

mechanisms: reptation and 'jumps' due to breakage and recombination, this theory predicts an exponent of $-\frac{5}{3}$. When the micelles become very long, other processes (possibly breathing or Rouse motion) are dominant, and give rise to an approximately concentration-independent self-diffusion coefficient.

This work was supported in part by the Swiss National Science Foundation (NF-19).

References

[1] Cates M E 1987 *Macromolecules* **20** 2289
[2] Cates M E 1988 *J. Physique* **49** 1593
[3] Candau S J, Hirsch E, Zana R and Adam M 1988 *J. Colloid Interface Sci.* **122** 430
[4] Candau S J, Merikhi F, Waton G and Lemarechal P 1970 *Preprint*
[5] Appell J and Porte G 1983 *J. Physique Lett.* **44** L689
[6] Candau S J, Hirsch E and Zana P 1985 *J. Colloid Interface Sci.* **105** 521
[7] Candau S J, Hirsch E and Zana P 1984 *J. Physique* **45** 1263
[8] Messager R, Ott A, Chatenay D, Urbach W and Langevin D 1988 *Phys. Rev. Lett.* **60** 1410
[9] Safran S A, Pincus P A, Cates M E and MacKintosh F C 1990 *J. Physique* **51** 503
[10] Scartazzini R and Luisi P L 1988 *J. Phys. Chem.* **92** 829
[11] Schurtenberger P, Scartazzini R, Magid L, Leser M E and Luisi P L 1990 *J. Phys. Chem.* at press
[12] Schurtenberger P, Scartazzini R and Luisi P 1989 *Rheologica Acta* **28** 372
[13] Schurtenberger P, Magid L J, Heenan R, Penfold J and Luisi P L 1990 in preparation
[14] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (London: Cornell University Press)
[15] Mukerjee P 1972 *J. Phys. Chem.* **76** 565
[16] Safran S, Turkevich L E and Pincus P 1984 *J. Physique Lett.* **45** L69
[17] Blankschtein D, Thurston G and Benedek G B 1986 *J. Chem. Phys.* **85** 7268
[18] Gelbart W M, Ben Shaul A, Mac Mullen W E and Masters A 1984 *J. Phys. Chem.* **88** 861
[19] Axelrod D, Koppel D, Schlesinger J, Elson E and Webb W W 1976 *Biophys. J.* **16** 1055
[20] Davoust J, Devaux P F and Leger L 1982 *Mol. Biol. Organ. J.* **1** 1233
[21] Lanni F and Wave B R 1982 *Rev. Sci. Instrum.* **53** 9005
[22] Ott A, Bouchaud J P, Urbach W and Langevin D 1990 submitted