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ORIGINAL CONTRIBUTION

F. Aliotta
M. Sacchi

Living polymers and polymer solutions: a misleading analogy

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Dr. F. Aliotta (✉) · M. Sacchi
Istituto di Tecniche Spettroscopiche del CNR
Salita Sperone 31
98166 Messina, Italy
E-mail: aliotta@hpits1.me.cnr.it

Abstract Experimental results from colloidal suspensions of worm-like micelles are currently interpreted in terms of close analogies between this kind of systems and polymeric solutions. In particular, it was hypothesized that the viscoelastic properties of dense systems of giant flexible cylindrical micelles can be rationalized in terms of an entangled network of worm-like aggregates, very similar to a neutral random polymeric network. Such an idea is strongly supported by theoretical results that, in a mean-field approximation, suggests for an unlimited growth process of the micellar contour length with concentration. The mean-field theory indicates for an exponentially shaped length distribution function, with mean $\langle L \rangle$ depending on concentration, ϕ, in agreement with a scaling law $\langle L \rangle \propto \phi^{\alpha}$ ($\alpha = 0.5$ in the simpler approach). A number of experimental results seem to be successfully interpretable within this framework.

Aim of this work is to show that the agreement between theory and experiment is just an accident, being the mean-field approach, in principle, inadequate in describing systems dense enough to show a concentration dependence of the mean micellar size. It will be unambiguously shown that there is no way to describe semi-diluted micellar solutions through a mean-field approximation and that there does not exist any scaling law of the kind $\langle L \rangle \propto \phi^{\alpha}$. Furthermore, it will be shown that the shape of the size distribution function is markedly different from the exponential one. The basis for a more realistic approach for the growth process of micellar aggregates is also presented and some preliminary indications are successfully compared with experimental results.

Key words Living polymers – gels – reverse micelles

Introduction

It is now well established that, under certain conditions, micelles existing in aqueous solutions tend to grow and that such a growth process is driven by a number of experimental parameters, among them are temperature, concentration and pressure. In a number of systems, the growth process can take place anisotropically, changing the shapes of the micellar aggregates from sphere to rods, cylinders or highly flexible worm-like aggregates.

In the years 1980–1982, some magnetic birefringence and light-scattering experiments strongly supported the idea of very long flexible micelles [1–3] and some analogy between such kind of systems and polymer solutions was, for the first time, proposed. The idea was immediately

confirmed by the theoretical prediction, for microemulsions, of the existence of polymer-like phases [4], associated with the formation of long flexible cylinders. On this basis, light-scattering results from cylindrical micellar solutions [5] were easily interpreted in terms of an entangled network of worm-like aggregates.

At the same time, the difference between these systems and conventional polymer solutions was quite evident: micelles are not static objects but dynamical entities continuously breaking and reforming. Accounting for such a consideration, it became usual to refer to these systems as *living polymers* or *equilibrium polymers*.

While the average static properties of these colloidal systems can be adequately described in terms of conventional models for polymer solutions, the interpretation of the observed dependence of the viscosity by concentration requires some modification of that theory. For semidilute polymer solutions, the diffusional properties are well described by the de Gennes reptation theory [6, 7] in which the stress relaxation process is dominated by the reptation time, the time that a chain takes to fully disengage itself from its original environment. The leading idea is that, for worm-like micelles, the relaxation of the viscous drag is driven by the competition between the reptation time and the lifetime of the aggregate under consideration. The de Gennes model can be adopted after the dependence of the mean chain length by concentration is known. Of course, the mean micellar size distribution function should be determined by the kinetic equilibrium between the breaking and reforming processes.

Cates developed a mean-field model [8, 9], based on the above considerations and on the following assumptions:

a) The length, L, of the chain is treated as a positive and continuous variable. This means that the adopted space of configurations is the space R^+ [10].

b) The observable L is weighted by the number density $N(L)\,\mathrm{d}L$, the number of chains of length $L \pm \frac{1}{2}\mathrm{d}L$ existing in the total volume V. Such a choice for the density characterizing our thermodynamic system will imply the following N *measure* of the set R^+:

$$\mu_N(R^+) \int_0^{+\infty} N(L)\,\mathrm{d}L = \frac{N_{TOT}}{V}\,, \tag{1}$$

where N_{TOT} is the total number of objects existing in the volume V.

c) A chain can break everywhere along its length, with uniform probability per unit time and unit length.

d) The reverse reaction proceeds at a rate that is proportional to the product of the concentrations of the two reacting sub-chains and is independent of their molecular weights.

e) Successive breakage and recombination events for a given chain are *AND* events. This means that there is no higher probability for a chain end to link up with the chain from which it was recently detached than with other chain ends in the vicinity.

Under these assumptions, the equation governing the time dependence of the number density of chains of length $L \pm \frac{1}{2}\mathrm{d}L$ is written as

$$\dot{N}(L) = -c_1 L N(L) - c_2 N(L) \int_0^{+\infty} N(L')\,\mathrm{d}L' + 2c_1 \int_L^{+\infty} N(L')\,\mathrm{d}L' + c_2 \int_0^{+\infty}\int_0^{+\infty} N(L')N(L'')\delta(L' + L'' - L)\,\mathrm{d}L'\,\mathrm{d}L''\,. \tag{2}$$

In Eq. (2), the first term represents the decrease in $N(L)$ by breakage, the second is the decrease by reaction of chains of length L with others to form longer chains, the third takes into account for creation of chains of length L by breakage of longer chains (the factor 2 comes from the occurrence of two equivalent possibilities for breakage) and the last term describes the reaction of two shorter chains to produce one of length L. The parameters c_1 and c_2 are rate constants for the two reactions whose dimensions are $[\mathrm{m}^{-1}\,\mathrm{s}^{-1}]$ and $[\mathrm{m}^3\,\mathrm{s}^{-1}]$, respectively.

The steady-state solution ($\dot{N}(L) = 0$) for Eq. (2) is easily obtained:

$$N(L) = \frac{2c_1}{c_2}\exp\left(-\frac{L}{\langle L\rangle}\right). \tag{3}$$

The next step is to derive the dependence of the mean chain length $\langle L\rangle$ from the volume fraction of the dispersed phase, $\phi = V_P/V$ (where V_P is the total volume of polymeric chains). If one indicates by σ the cross-sectional area of chains (implicitly assumed ϕ independent), it follows:

$$\phi = \sigma \int_0^{+\infty} LN(L)\,\mathrm{d}L = \frac{2\sigma c_1}{c_2}\langle L\rangle^2, \tag{4}$$

which immediately gives

$$\langle L\rangle \propto \sqrt{\phi}\,. \tag{5}$$

The obtained dependencies of $\langle L\rangle$ on ϕ and T can be inserted in the de Gennes model to reach the proposed goal. It was deduced the existence of different regimes, essentially determined by the ratio reptation-time/breaking-time, as well as some qualitative indications for the dependence of the viscosity by such a quantity.

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The approach appeared to be convincing and the model was successfully adopted by everybody working in the field. As an example, we will remind the paper by Messager et al. [11], where the first self-diffusion measurements on elongated micelles in the semidilute regime, performed with fringe-pattern photobleaching-recovery techniques, are reported and compared with the Cates indications and suggestions from a modified version of that model to include at least excluded volume interactions [12].

When the formation of gel-like, viscoelastic phase was discovered in the soybean lecithin/organic solvent/water system [13], the interpretation of the observed phenomenon in terms of a polymer-like entangled network of giant flexible worm-like micelles followed naturally. Its fascinating behavior (the formation of a gel-structure without any chemical cross-linking among chains) made this kind of systems the prototype for *living polymers*. A number of papers have earned their place in the literature by this topic, all interpretation successfully within the polymer-like frame [14].

Aim of this paper is to show that, in spite of the apparent good agreement between a number of experimental results and theory, some other experimental indications suggests for a different point of view. Furthermore, we will show how, from a critical revision of the currently adopted approach, it is possible to see that it is, in principle, inadequate to describe the experimentally observed concentration dependence of the micellar contour length and we will give some indications for a possible alternative way to formulate more suitable models, able to take into account the complex nature of *living polymers*.

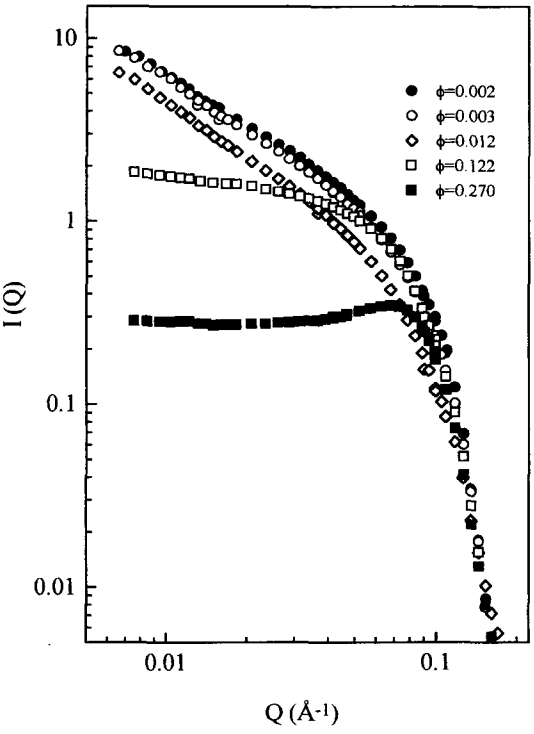

Fig. 1 Experimental $I(Q)$ vs Q curves, scaled with concentration, for soybean lecithin/d_{12}-cyclohexane/water systems at fixed water content, $w_0 = 10$, and temperature $T = 20\,^{\circ}C$, at different values of the volume fraction, ϕ, of the dispersed phase

Discrepancies between theory and experiments

In a recent paper [15], we have shown that some small angle neutron scattering (SANS) results from d_{12}-cyclohexane/lecithin/water systems are not interpretable within the framework of the polymer-like approach. The situation is well depicted by the scattering profiles for systems at fixed water content, $w_0 \cong 10$ (w_0 is the number of water molecules per lecithin molecule), and at different volume fractions, ϕ, reported in Fig. 1 (data obtained on the V4 instrument at the Berlin Neutron Scattering Center). Just brief inspection of the figure is enough to see that the experimental data overlap at high wave-vector values, suggesting for a ϕ-independent cross-sectional radius of about 30 Å. If one would compare our results from the diluted samples ($\phi < 0.012$) with previous SANS indications [16], it becomes easy to see that the two sets of data could be interpreted within the same conventional approach: an increase of concentration will induce an unidimensional (and unlimited) growth of the worm-like micelles. But the appearance of a strong interference maximum in the $I(Q)$ vs Q curve at the highest concentration explored ($\phi = 0.270$) represents an unexpected result. Such an observation is not consistent with the working hypothesis of a random gel-like phase of entangled worm-like micelles, that should be characterized by a Lorentzian structure factor. It is clear that the above result represents an interesting challenge to the current theory, but it is also evident that it is not enough to reject the proposed model.

A further indication against the proposed model can be obtained by an inspection of Fig. 2, where we report some of the results analyzed in Ref. [15]. The data in Fig. 2 refer to two sets of samples at $w_0 = 0$ (Fig. 2a) and $w_0 = 12.2$ (Fig. 2b), at $T = 20\,^{\circ}C$ and at several ϕ values. Data from the set at $w_0 = 0$ are easily interpreted. In this case, in fact, we are in the presence of conventional reverse micellar solutions of spherical lecithin aggregates dispersed in oil: following suggestions from Ref. [13], the sphere-to-rod transition will be induced by addition of small quantities of water; successive addition of water will induce the growth of rods into giant flexible cylinders. On this respect, "lecithin water-in-oil microemulsions represent a unique system which shows a characteristic sphere-to-rod

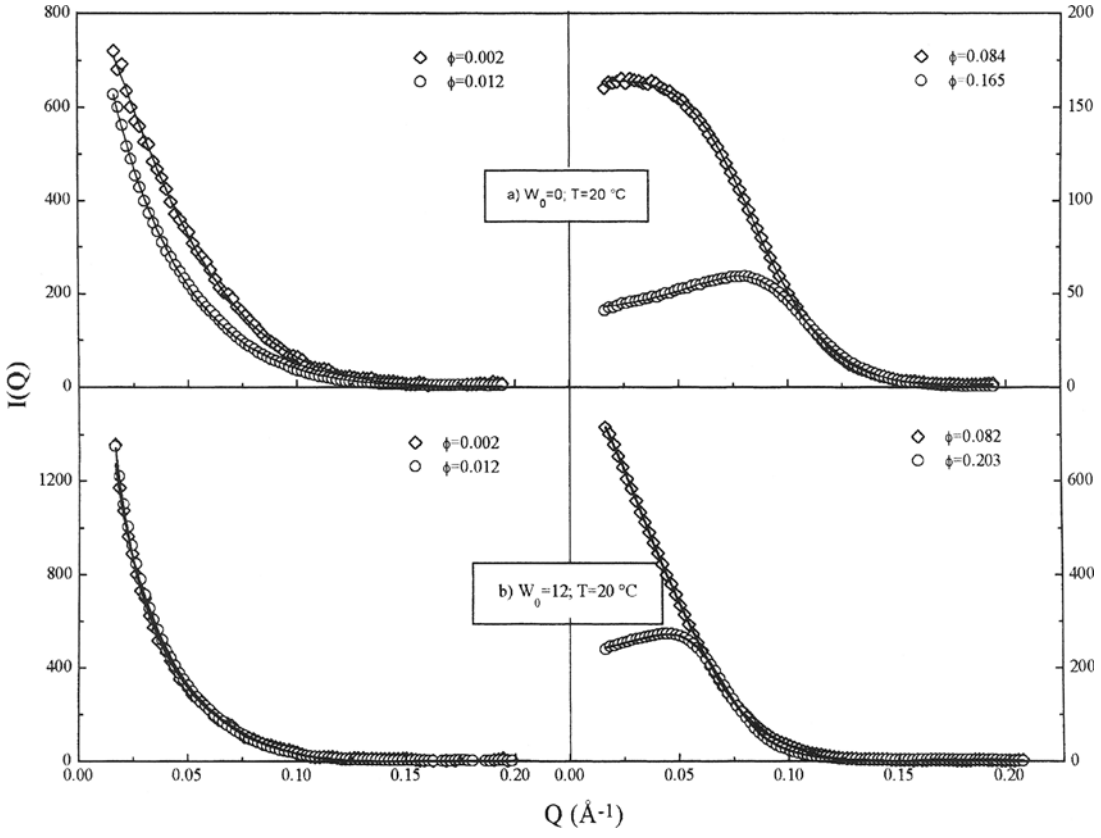

Fig. 2 Normalized small-angle neutron scattering results from soybean lecithin/d_{12}-cyclohexane/water systems (data from Ref. [15]). Continuous lines: fitting results (see text)

transition normally observed in aqueous solutions only" [14]. The appearance of a strong interference maximum is not surprising for a dense system of spherical micelles. If one assumes a spherical form factor for the micellar aggregates and a hard sphere interaction for the structure factor contribution, the experimental data could be reproduced after the appropriate expression for the size distribution function is found. In Ref. [15], we adopted the following fitting law [17]

$$I(Q) \propto P(Q) \frac{1}{1 + 8(v_0/v_1) \cdot \varepsilon \phi(DQ)}, \tag{6}$$

where ε is a constant that, in practice, can be taken equal to 1, v_0 is the volume of the interacting particle, v_1 is the average volume assigned to each particle, $\phi(QD)$ is the potential energy function and D the average micellar distance. $P(Q)$ is the scattering form factor for polydisperse spherical particles with size distribution function $n(R)$,

$$P(Q) \propto \int_0^\infty \int_0^\infty \sqrt{n(R_1) n(R_2)}\, \Phi(QR_1) \Phi(QR_2) \times \delta(R_1 - R_2)\, dR_1\, dR_2 . \tag{17}$$

The $\Phi(x)$ functions in (6) and (7) are given by

$$\Phi(QR) = 3 \frac{\sin(QR) - QR\cos(QR)}{Q^3 R^3},$$

and $n(R_1)$, $n(R_2)$ represent the number densities for particles of radius R_1 and R_2, respectively. In Ref. [15], it was shown that data from concentrated solutions cannot be fitted consistently with an exponentially shaped size-distribution function. As a consequence, a Weibull density function was tentatively adopted as the size-distribution function

$$n(R) = A(R/\bar{R})^{b-1} \exp[-(R/\bar{R})^b]$$

that could be adequate since it collapses to a simple exponential behavior when the parameter b equals 1 while, for increasing b, turns to a localized distribution around the mean value $\bar{R}$. It was assumed that an increase in the parameter b at values significantly higher than 1 marks the transition from a regime in which the growth of the micellar radius is just driven by equilibrium kinetics to a new one, where excluded volume effects play a major role. The continuous lines in Fig. 2a represent the fitting results with

Table 1 Results of the fitting procedure with polydisperse interacting hard sphere model for samples at $w_0 = 0$

ϕ	$\bar{R}$ (Å)	D (Å)	b	$8v_0/v_1$
0.002	26.3	—	1.0	—
0.012	54.4	—	1.0	—
0.084	35.8	61.4	5.6	1.1
0.165	24.6	54.5	5.8	2.6

$\bar{R}$, mean micellar radius; D, mean intermicellar distance; b, $8v_0/v_1$, see text.

Eq. 6 (see Table 1 for the corresponding fitting parameters), while in Fig. 3 the corresponding $n(R)$ distributions, as obtained by the fitting procedure, are plotted (the corresponding experimental profiles are reported in the inset, in a log–log plot).

The behavior of the data in Fig. 2a was rationalized as follows:

i) At low values of the volume fractions, the mean micellar radius is ϕ-dependent, with a scaling-law essentially determined by the kinetic equilibrium between breaking and reforming mechanisms;

ii) Above a critical volume fraction, excluded volume effects play an increasingly important role; now, polydispersity is strongly dependent on ϕ and the micellar growth process is hindered by intermicellar interactions;

iii) At very high values of the volume fractions, a preferred micellar size is established with a consequent preferred intermicellar correlation distance (or of a preferred mesh size for the most probable percolated structure).

In Ref. [15], we showed, on a thermodynamic basis, how excluded volume interactions can affect the micellar size distribution, and we concluded that the assumption of a system polydispersity independent of concentration is a suitable working hypothesis only within the limits of applicability of a mean-field approach, i.e., for highly diluted systems.

In interpreting the data in Fig. 2b, one should take into account the theoretical indication, supported by a number of experimental results [13, 14, 16], suggesting for a unidimensional growth of the micelles upon addition of water. At the same time, the close similarity between the two sets of data reported in Figs. 2a and b suggests the existence of strong limitations, imposed by intermicellar interactions, on the growth process of the cylindrical aggregates.

Following the above considerations, the data reported in Fig. 2b were fitted by Eq. 6, where a core-shell model was adopted for the form factor of the cylinders [18]

$$P(Q) \propto \int_0^{\pi/2} \sin\beta |(\rho_1 - \rho_2) V_a G(Q, \beta, a) + (\rho_2 - \rho_0) V_b G(Q, \beta, a)|^2 \, d\beta \,, \quad (8)$$

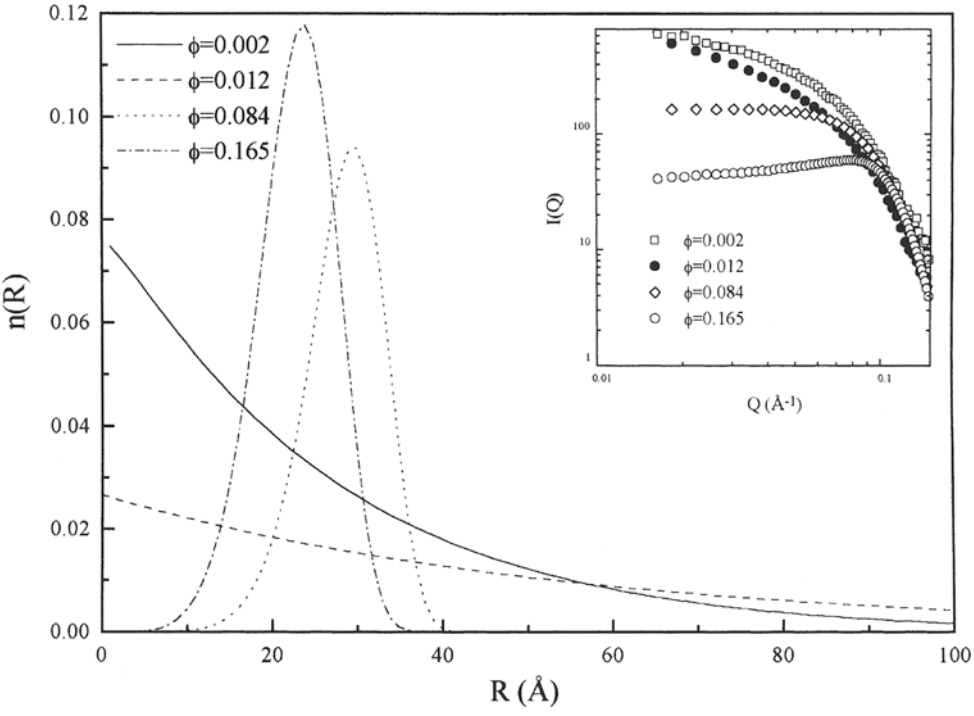

Fig. 3 Micellar size distribution functions, for samples at $w_0 = 0$, $T = 20\,^{\circ}C$ and at different ϕ values (as obtained from the fitting procedure in Ref. [15]). Inset: corresponding scattering profiles in log–log plot

Table 2 Results of the fitting procedure with core-shell cylindrical model and hard-sphere interaction for d_{12}-cyclohexane/lecithin/water systems at different concentrations. $w_0 = 12.2$, $T = 20.2\,^{\circ}C$

ϕ	b (Å)	a (Å)	L (Å)	D (Å)	$8v_0/v_1$
0.002	36.9 ± 0.3	27.1 ± 0.2	1440 ± 36	—	—
0.012	40.0 ± 0.3	27.6 ± 0.2	1570 ± 39	157.0	0.21
0.082	40.4 ± 0.3	28.5 ± 0.2	163 ± 4	103.7	0.70
0.203	38.8 ± 0.3	28.3 ± 0.2	81 ± 2	81.0	1.99

a, inner core radius; b, outer shell radius; L, average micellar length; connected structure correlation distance; $8v_0/v_1$, see Eq. (2).

where ρ_1, ρ_2 and ρ_0 are the neutron scattering length densities of the inner cylinder, outer coating and solvent, respectively, a and b are the core radius and the outer radius of the micelles, V_a and V_b represent the core and the micelle volumes. The function $G(Q, \beta, x)$ is defined as

$$G(Q, \beta, x) = \frac{\sin(QH\cos\beta)2J_1(Qx\sin\beta)}{(QH\cos\beta)(Qx\sin\beta)},$$

where $H = L/2$, J_1 is the first-order Bessel function and β is the angle between the Q-vector and the axis of the micelles.

In spite of some limitations in the adopted fitting procedure (see Ref. [15] for further details), the experimental data turned out to be well reproduced (see continuous lines in Fig. 2b). The almost overlapping scattering profiles from lower concentration samples (Fig. 2b left) should be an immediate indication of the existence of very large aggregates (the differences between the two sets of data should be larger at Q values lower than those allowed by the neutronic probe) while the intensity behavior from higher concentration samples (Fig. 2b on the right) strongly suggests for the establishment of a preferred size, induced by excluded volume effects (see Table 2).

We are conscious that the adoption of Eq. (6) to describe reversible colloidal aggregation is questionable. In Ref. [15], it was pointed out how the local arrangement of spherical particles described by Eq. (6) could not be extended to dense systems too literally; in such a situation the system could be described more adequately in terms of a percolated structure (in Ref. [15] we proposed a bicontinuous structure) with obvious reinterpretation of the fitting parameters. A more correct approach to the problem would be to avoid any assumption of an analytical expression for the unknown interparticles structure factor, and in extracting experimentally the size averaged $\langle S(Q)\rangle$ using previous knowledge of $\langle P(Q)\rangle$ [19]. In our case, some information about $\langle P(Q)\rangle$ can be gained from the previous data analysis for diluted samples and after the assumption of a spherical micellar shape with no respect of the concentration. This last assumption is necessary due to the fact that, in the analysis of the scattering data, it is almost impossible to distinguish between the asymmetry

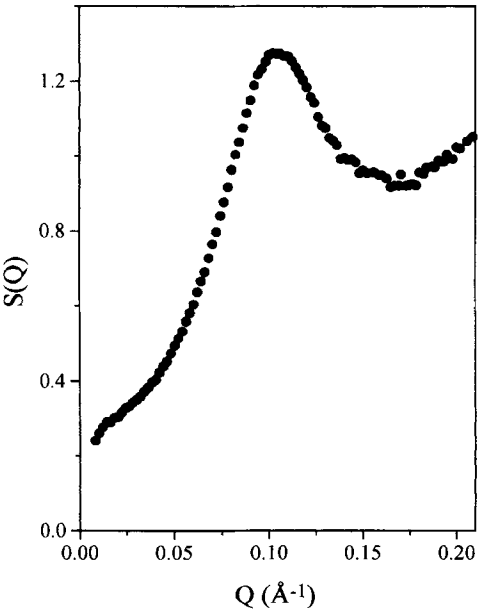

Fig. 4 Interdroplet structure factor extracted from SANS data at $\phi = 0.165$ and $w_0 = 0$

of the domains and their polydispersity, in the absence of independent evidence for one or the other.

In Fig. 4, the interdroplet structure factor, extracted from SANS data at $w_0 = 0$ and $\phi = 0.165$ at $T = 20\,^{\circ}C$, assuming an average micellar radius of 24.6 Å, is reported as an example. If one compares the data in Fig. 4 with the results reported in Ref. [19] for AOT/water/decane reverse micelles, it is immediate to observe how for the lecithin in cyclohexane micelles the values of $\langle S(Q = 0)\rangle$ is not very low, suggesting for an interparticle repulsive interaction not so strong as observed for the AOT-based systems, and resulting in higher osmotic compressibility. The obtained structure factor is characterized by a first diffraction peak of height ~ 1.28, centered at $Q \sim 0.103$ Å^{-1}, followed by a second smoothed peak that could be roughly estimated as centered at $Q \sim 0.21$ Å^{-1}. Furthermore, it should be stressed that the above-described feature of the obtained structure factor (i.e., the existence of a sharp diffraction

peak followed by a second one occurring at approximately twice the Q-position of the first) is characteristic of a dense liquid-like structure. It is possible to obtain an estimation of the average interparticles distance D, from the Q-position of the first diffraction peak, Q_{max}, according to an empirical formula, valid in describing correlation peaks in dense micellar systems [20]

$$Q_{max}D = 6.8559 + 0.0094D.$$

In this way, we obtain $D \sim 73$ Å, that, taking into account for the large error introduced in the procedure adopted to extract the $\langle S(Q)\rangle$ curve from experimental data, is not too much larger than twice the $\langle R\rangle$ value hypothesized.

Furthermore, it should be observed that the existence of a scattering peak is an usual feature for microemulsions or micellar solutions at high enough concentrations, and different models have been proposed to relate the peak position, Q_{max}, to the characteristic size, d, of the phase scattering. As an example, Teubner and Stray [21], on the basis of thermodynamic arguments, have calculated the following scattering function:

$$I(Q) = \frac{a_1}{a_2 + a_3Q^2 + a_4Q^4}. \tag{9}$$

In Eq. (9), the parameters a_i can be written in terms of Q_{max}, $I(Q_{max})$, $I(0)$ and of the mean-square fluctuation of the scattering density, leading to an expression

$$I(Q) = \frac{I(0)}{(1-(I(0)/I(Q_{max})))((Q^2/Q_{max}^2)-1)^2 + I(0)/I(Q_{max})}. \tag{10}$$

From the correlation function leading to Eq. (9), two length scales can be deduced: a distance d, characteristic for the domain size (the periodicity) and a correlation length ξ.

In Fig. 5, experimental data for samples at $w_0 = 0$ and $w_0 = 12$, at the maximum concentrations explored, are reported in a log–log plot and fitted to Eq. (10) (dashed lines; see Table 3 for the resulting fitting parameters). The obtained ξ values turn out in good agreement with the corresponding values for $\bar{R}$ and L reported in Tables 1 and 2, respectively, supporting for a reinterpretation of these latter, as reported above. On the contrary, the d values differ from those (D) obtained through Eq. (6) (and also from the value deduced by the structure factor contribution extracted for samples at $w_0 = 0$). Finally, it is easy to observe how the experimental data are better fitted with Eq. (6) (continuous lines in Fig. 5) than with Eq. (10), indicating that a three-parameter fit is not adequate to reproduce the experimental scattering profiles.

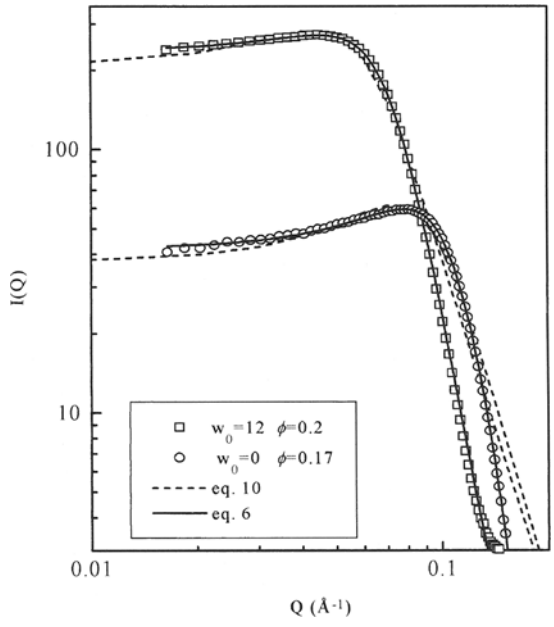

Fig. 5 Log–log plot of the scattering profiles for samples at $w_0 = 0$ and $w_0 = 12$ at the maximum concentrations investigated

Table 3 Results of the fitting procedure with Eq. (10)

w_0	ϕ	$I(0)$	$I(Q_{max})$	Q_{max}	ξ	d
0	0.165	37.5	61.6	0.073	24.8	33.2
12	0.203	209.6	284.5	0.044	75.0	118.4

In summary, it should be noticed how all the above reported points of view are suggesting that the presence of a peak in the scattering profiles can be understood only if the system is described as a usual micellar solution and not in terms of analogies with polymeric solutions. While results from diluted samples could be interpreted within the framework of the current theory, indicating a mean micellar length scaling with ϕ^{α}, SANS from highly concentrated systems do not agree with the working hypothesis of a polymer-like network of entangled worm-like micelles.

It is to be stressed that the same indication comes from a NMR study on lecithin microemulsions gels [22]. In that work it was pointed out that, during the gel formation process, water mobility increases and, contrary to the expectation of the established model, no evidence of fatty chains entanglements is found. The authors concluded that entangled chains fully constrained, as in semidilute polymer solution, seem improbable.

Following the above-reported experimental results, the only possible conclusion is that the existence of worm-like micelles able to grow-up monotonically over distances

higher than the entanglement length is not confirmed and that the hypothesis of polymer-like entangled networks should be definitely refused.

Maximum entropy approach

The main criticism against the established model is concerned with its description of an unlimited micellar growth process with ϕ. In particular, the model seems to indicate that the average volume of our aggregates, exponentially distributed according to Eq. (3), would take its maximum value at the maximum allowed concentration. It appears quite evident that, when concentration increases, the free volume in our system decreases, so there is not enough room for the hypothesized growing-up process. Furthermore, at intermediate concentrations, when excluded volume effects are no more negligible, the adopted mean-field theory appears to be too a crude approximation, particularly if one would take into account for the existence of very long chains. In addition, when the concentration increases, many particle interactions could take place at high rate enough to be reflected in the true concentration dependence of the average chain length.

Really, there exists a more direct issue against the result furnished by Eq. (4). In fact, from the above arguments it should be clear enough that Eq. (2) must be assumed just as a first approximation at infinite dilution. The extrapolation of this approach (i.e., of this dependence of the growth process on the volume fraction) to finite concentrations, need not be successful.

Let us try to follow the path leading to the claimed ϕ-dependence of $\langle L\rangle$. Equation (4) is written and then the integral is performed, after substitution of Eq. (3) for $N(L)$. But, such an operation implies the forgetting of the previous implicit assumption (Eq. (1)). It can be easily realized that the integral in Eq. (4) should be performed in the following way:

$$\int_0^{+\infty} LN(L)\,\mathrm{d}L = -\langle L\rangle LN(L)\big|_0^{+\infty} + \langle L\rangle \int_0^{+\infty} N(L)\,\mathrm{d}L = \int_0^{+\infty} N(L)\,\mathrm{d}L, \tag{11}$$

so Eq. (4), taking into account for Eq. (1), should be written:

$$\phi = \sigma \int_0^{+\infty} LN(L)\,\mathrm{d}L = \sigma\langle L\rangle \int_0^{+\infty} N(L)\,\mathrm{d}L = \sigma\langle L\rangle \frac{N_{\mathrm{TOT}}}{V}. \tag{12}$$

If one forgets the normalization condition given by Eq. (1), it seems possible to write the quantity N_{TOT}/V in terms of $\langle L\rangle$; but such a procedure is just a circular path.

Taking into account for the ϕ definition, Eq. (12) becomes

$$V_{\mathrm{p}} = \sigma\langle L\rangle N_{\mathrm{TOT}}, \tag{13}$$

indicating the trivial proportionality, at fixed $\langle L\rangle$, between the total number of aggregates and the volume they are occupying. A simpler way to detect the problem can be found in dividing both members of Eq. (4) by the same quantity $\int_0^{+\infty} N(L)\,\mathrm{d}L$:

$$\sigma \frac{\int_0^{+\infty} LN(L)\,\mathrm{d}L}{\int_0^{+\infty} N(L)\,\mathrm{d}L} = \sigma \frac{2(c_1/c_2)\langle L\rangle^2}{\int_0^{+\infty} N(L)\,\mathrm{d}L}, \tag{14}$$

which, remembering the definition of $\langle L\rangle$, reduces to a tautology.

The sources of the logic trap stay in the choice of the number density for the characterization of the system. It is easy to observe that Eq. (2) maintains the same meaning after Eq. (1) is substituted with

$$\int_0^{+\infty} N(L)\,\mathrm{d}L = 1, \tag{15}$$

that implies $N(L)\,\mathrm{d}L$ is now the population of chains with length $L \pm \frac{1}{2}\,\mathrm{d}L$. The time evolution of the population will be again expressed by Eq. (2), when the rate constants c_1 and c_2 take the new dimensions $[\mathrm{m}^{-1}\,\mathrm{s}^{-1}]$ and $[\mathrm{s}^{-1}]$, respectively. From maximum entropy considerations, it can be found that the stationary population is given by

$$N(L) = Z^{-1}\exp(-vL), \tag{16}$$

where

$$Z = \int_0^{+\infty} \exp(-vL)\,\mathrm{d}L.$$

The parameter v is implicitly defined by

$$\langle L\rangle = \frac{\int_0^{+\infty} L\exp(-vL)\,\mathrm{d}L}{\int_0^{+\infty} \exp(-vL)\,\mathrm{d}L} = \frac{1}{v}. \tag{17}$$

Combining Eqs. (16), (17) and (3) (where c_1 and c_2 are expressed in the new dimensions), it immediately follows

$$\langle L\rangle = \frac{c_2}{2c_1}, \tag{18}$$

clearly showing that the mean-field model is only describing the $\langle L\rangle$ dependence on temperature through the two rate constants.

The configurational entropy dependence on c_1 and c_2 can be evaluated:

$$H[N(L)] = -\int_0^{+\infty} N(L)\ln[N(L)]\,dL = \ln\left[1 + \ln\left(\frac{c_2}{2c_1}\right)\right]. \tag{19}$$

Summarizing, we claim that while an exponential size distribution function, obtained in a mean-field approximation, can be adopted as an approximate solution at low enough concentrations, the currently accepted ϕ-dependence of $\langle L\rangle$ was erroneously deduced. The result given by Eq. (18) is an immediate consequence of the a priori assumption of an unlimited growth process for the aggregates. In other words, Eqs. (18) and (19) are the obvious consequence of the choice of the R^+ space as our space of configurations.

Now, it becomes easy to show which kind of mechanism could be the source of the experimentally observed ϕ-dependence of $\langle L\rangle$.

Would our space be the R^+ sub-space $[L_1, L_2]$, Eq. (14) becomes

$$N(L) = \frac{\exp(-vL)}{\int_{L_1}^{L_2}\exp(-vL)\,dL}, \tag{20}$$

where v is given by

$$\langle L\rangle = \frac{\int_{L_1}^{L_2} L\exp(-vL)\,dL}{\int_{L_1}^{L_2}\exp(-vL)\,dL} = \frac{1}{v} + L_1 + \frac{L_1 - L_2}{\exp[-v(L_1 - L_2)] - 1}, \tag{21}$$

which can be solved numerically. Equation (21) gives a direct indication that the complex behavior of the system is the consequence of the existence of some constraints to the micellar growth process. With the choice of a limited configurational space, the values of $\langle L\rangle$ can span over the set $[L_1, L_2]$. Of course, configurational entropy will be zero at the two limits and, because entropy is a strictly concave function, it will assume its maximum value for an intermediate length inside the given interval, in agreement with Eq. (21). The meaning of L_1 is soon rationalized as the size of the smallest objects existing in our system (monomers) while L_2 will be determined by excluded volume effects. The L_2 value will not be a constant for the system but it will be a function of T (through the rate constant values), ϕ and time (through the instantaneous population distribution). The time dependence of L_2 will represent the feedback effect driving the time evolution of the population. A change of L_2 will cause a change in $\langle L\rangle$ and such a consideration should be enough to identify $\langle L\rangle$ as a collective property of the system.

It is the introduction of such a feedback which allows for talking about competition among different species.

It is such a feedback effect that makes the difference between this kind of system and a conventional polymeric solution.

The only analogy one can detect between *living polymers* and *polymer solutions* stays in the trivial observation of the existence of linear units in both systems. But it is, in principle, wrong to carry on with this analogy so as to include the macroscopic properties of the systems, such as network structures or viscosity. In particular, from both experimental results and theory, it appears quite evident that there is no meaning in proposing the existence of entangled networks of *living polymers* (at least, if the possibility is excluded of a lifetime for very long chains which is much longer that their reptation time, that would reduce *living polymers* to *polymers*).

Numerical results

To test the validity of the above-reported working hypothesis, we tried to formulate a model able to describe the system as a whole, at least in its more significant aspects. The details about the involved mathematics are over the aim of this paper and will be given in a future article.

In any case, the main points of the model, based on the iterative application of a Markov operator mapping points of the space $[L_1, L_2(t)]$ into space $[L_1, L_2(t + dt)]$, could be summarized as it follows:

a) The dynamical evolution of the system is described looking at the time dependence of the population of the existing different species (chains) and monitoring the time evolution of the configurational entropy;

b) Chains can break everywhere with uniform probability;

c) The reforming event takes place with a constant efficiency but the probability that two chains meet is given by the product of their populations weighted by their molecular weights (or their volumes);

d) In the process describing the creation of a chain of length L, we are taking into account all possible interactions (within a time interval dt) giving rise to such a result. This means that we account for all the possible reactions from $2, 3, \ldots, n$-bodies interactions, up to a maximum n, given by the aggregation number of the chain of length L;

e) The maximum allowed chain length is finite, being determined by considerations about a maximum packing factor for our aggregates (depending on their shapes).

The last point e) fulfils the requirement that the maximum allowed length is a function of ϕ, T and time. It is not

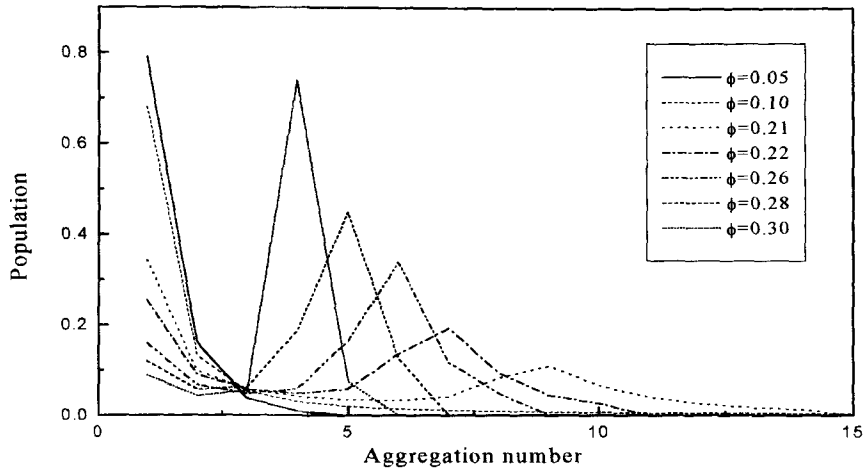

Fig. 6 Numerical results: size distribution functions at different concentrations. Rate constants and packing factor are the same through all the data

possible to give an analytical solution for our model, it being intrinsically a non-linear model. We can only follow what it is happening in our system when, given the initial conditions, we leave our dynamic law at working, mapping points of space at the time t into new points at the time $t + dt$.

The results from the iterative calculation turned out to be consistent with experiments. In Fig. 6, some examples for the resulting asymptotic equilibrium distribution functions are reported. It is manifest that, at low concentrations, the obtained size-distribution function is exponentially shaped while, when concentration increases, excluded volume effects drive the appearance of a preferred micellar size (the good agreement, at least from a qualitative point of view, with Fig. 3 should be noted). In Fig. 7, the dependence of the equilibrium configurational entropy, $H[N(L)] = -\sum_L N(L)\ln[N(L)]$, on $\ln[c_1]$ (Fig. 6a) and on ϕ (Fig. 6b) is reported. From an inspection of Figs. 6 and 7, the role played by the introduction of a dynamical cut-off in the maximum allowed chain size, determined by the instantaneous size distribution of our aggregates becomes evident. It is such an ingredient that, representing a feedback effect in the described iterative process, induces the existence of a preferred size at high concentrations, with the subsequent lowering of the equilibrium configurational entropy. Furthermore, it should be noticed that, at very low ϕ values, the model gives a length-distribution function independent of ϕ. This result is not surprising, since, under high dilution, our model has to reduce to Eq. (16).

Finally, the ϕ-dependence of the calculated equilibrium $\langle L \rangle$ value is reported in Fig. 8, at two different c_1 values. In the same figure, the continuous lines represent the currently accepted $\phi^{1/2}$ scaling law. It is easy to

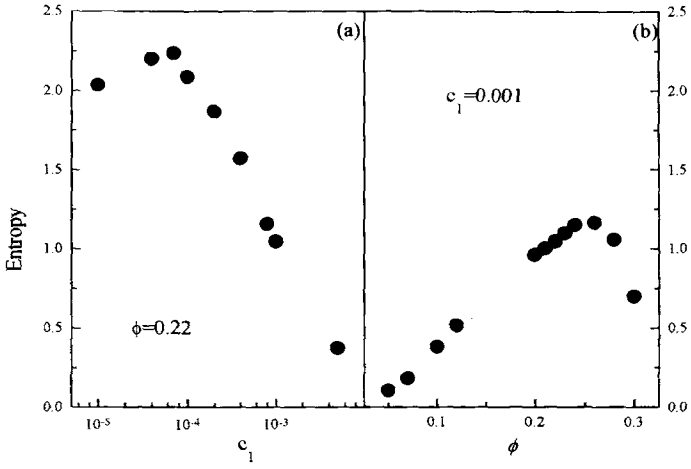

Fig. 7 Numerical results: configurational entropy dependence on $\ln(c_1)$ (a) and ϕ (b). Packing factor and c_2 rate constant are the same through the whole sets of data

observe that, in systems where the efficiency of the growing-up process is highly hindered by a very short lifetime for the chain bonds ($c_1 = 0.001$), a large concentration range exists in which the law $\langle L \rangle \propto \phi^{1/2}$ is apparently fulfilled. From Fig. 8, it is also evident that, in systems characterized by a higher efficiency for the growing-up process of the micelles ($c_1 = 0.0001$), the model predictions are suggesting for a higher scaling exponent (or for a situation in which the concentration-induced size-growth cannot be described by a single power law). This last indication should be compared with the experimental results reported in Refs. [14, 18] and can explain the discrepancies that the authors detected between their results and mean-field theory predictions.

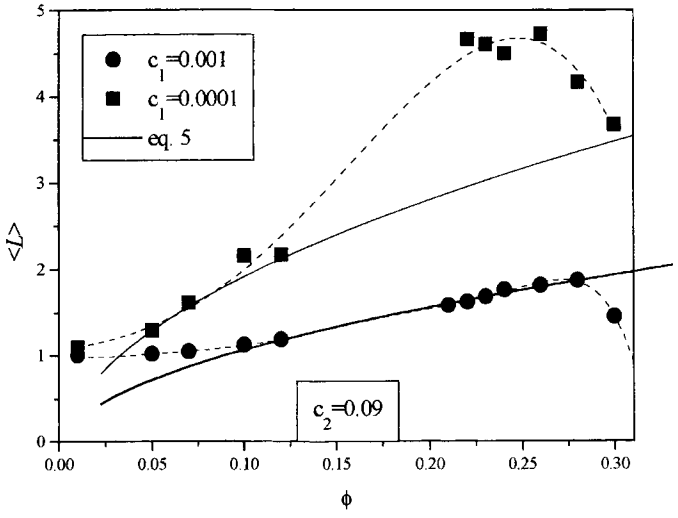

Fig. 8 Numerical results: ϕ-dependence of $\langle L \rangle$ at two different c_1/c_2 ratios. Continuous lines: $\phi^{1/2}$ law. Dashed lines: guides for eye

Discussion and conclusions

The results we obtained should not be surprising, they being the obvious consequence of the current definition for *living polymers*: solution of linear macromolecules that can break and recombine (see, e.g., Ref. [11]).

Such a definition implicitly suggests for some analogies between this kind of systems and the more conventional polymer solutions. The main difference stays in because for the latter, the size distribution function of the dispersed phase (i.e., the chain length polydispersity) is a static property, not depending on time, temperature or concentration.

This is not the case for *living polymers*. In such systems, in fact, the population of each specie present in solution will be determined by the competition between the breaking and reforming processes. As a consequence, we have to expect that the growth rate, for the population of the particular specie we are describing, should change in time, being it a function of the instantaneous population. If one waits enough to reach the stationary population, it should become clear that the steady-state solution of the problem is described by the kinetic equilibrium between the breaking and reforming processes: now, the decrease in the number of the members of our specie, due to the breaking process, is exactly compensated by the number of new members, born by the aggregation of objects with lower molecular weights (when the sum of the molecular weights of each object participating in the aggregation process is equal to the molecular weight of the specie of which we are following the evolution).

If one pays attention to the words used to describe the time evolution of the specie, it turns out that we are implicitly describing it as a conventional Verhulst or Volterra–Lotka dynamics [23]. If, in the system, only two species, are present, the total problem would be the analogous of the prey–predator problem. If one looks now at the system we named *living polymers*, it turns out quite clearly that the dynamics will be even more complex. In such a system, in fact, each specie is playing a double role: it is a prey for all the other species and, at the same time, it is their predator. This means that the instantaneous variation of the population of each specie will be a function of the instantaneous populations of all the others.

Concluding, we claim that the size distribution function at long times is an emerging complex property of the system, arising by the cross interactions among the different species. At the beginning of this discussion, it was asserted that the number of members of each specie is determined by the kinetic equilibrium between the breaking and reforming mechanisms but, now, it should be evident that such an equilibrium is not a local property, on the contrary, it is taking into account for the competition among all the existing species.

Summarizing, we can assert that when an experiment seems to indicate that some change in the mean chain length with concentration is taking place, such an occurrence should be clear evidence of a collective behavior that cannot be adequately described in a mean-field approximation. Nothing relevant can happen if aggregates are not interacting, due to the trivial consideration that no interaction means no competition (see Eq. (18)). Furthermore, in semi-dilute or concentrated micellar solutions, the dynamical process driving the long-time size-distribution function is a non-invertible (irreversible) process and, as a consequence, it is not, in principle, possible the use of the conventional thermodynamics of reversible processes as an heuristic method to deduce any property of our system.

It should be now clear how the differences between *polymer solutions* and *living polymers* are larger than one could, at first sight, imagine.

The different point of view adopted here, surely does not give the answers to all questions that have risen about *living polymers*. But, of course, it could represent the key to solving them. *Living polymers* did not reveal the proposed analogy with polymeric systems, on the contrary, they revealed to be just as any other conventional micellar solutions.

The new questions one could rise about them will be concerned with the wider class of dispersed solutions. And the role played by interactions would extend one's questions to the wider class of systems whose time evolution is driven by some kind of competition. From such a point of view, *living polymers* revealed to deserve the adjective *living* in a deeper sense then it was up to now understood.

At the same time, one should conclude that terms such as *living polymers* or *equilibrium polymers* must be deleted from the scientific language since they can lead to misguided attempts at connecting fundamentally different systems.

References

1. Porte G, Appell J, Poggi Y (1980) J Phys Chem 84:3105
2. Porte G, Appell J (1981) J Phys Chem 85:2511
3. Appell J, Porte G, Poggi Y (1982) J Colloid Interface Sci 87:492
4. Safran S, Turkevitch LA, Pincus P (1984) J Phys Lett 45:L-69
5. Candau SJ, Hirsh E, Zana R (1985) J Colloid Interface Sci 105:521
6. de Gennes PG (1971) J Chem Phys 55:572
7. de Gennes PG (1980) J Chem Phys 72:4756
8. Cates ME (1987) Macromolecules 20:2289
9. Cates ME (1988) J Phys France 49:1593
10. Really, in Ref. [9], L is treated as a discrete variable and the adopted configuration space is the space N. In any case, it can be easily observed that the two different choices are not implying any significative change in the theory
11. Messager T, Ott A, Chatenay D, Urbach W, Langevin D (1988) Phys Rev Lett 60:1410
12. Gelbart WM, Ben-Shaul A, MacMullen WE, Masters A (1984) J Phys Chem 88:861
13. Scartazzini R, Luisi PL (1988) J Phys Chem 92:829
14. Schurtenberger P, Cavaco C (1993) J Phys II France 3:1279, and references therein
15. Aliotta F, Fontanella ME, Sacchi M, Vasi C, La Manna G, Turco-Liveri V (1996) J Colloid Polym Sci 274:809
16. Schurtenberger P, Magid LJ, King SM, Lindner P (1991) J Phys Chem 95:4173
17. Guiner A, Fournet G (1955) Small Angle X-Ray Scattering. Wiley, New York
18. A core-shell model was adopted for the fitting procedure of data from the ternary systems, in view of the higher contrast between core and shell gained after the addition of water. In the case of samples at $w_0 = 0$, the fitting procedure was not able to distinguish between heads and tails of the surfactant molecules
19. Sheu EY, Chen SH, Huang JS, Sung JC (1989) Phys Rev A 39:5867
20. Chen SH, Sheu EY, Kalus J, Hoffmann H (1988) J Appl Crystallogr 21:751
21. Teubner M, Strey R (1987) J Chem Phys 87:3195
22. Capitani D, Rossi E, Segre AL, Giustini M, Luisi PL (1993) Langmuir 9:685
23. Volterra V (1931) Leçons sur la theories mathematique de la lutte pur la vie, Gauthier-Villairs, Paris. See also, Peitgen HO, Richter PH (1986) The Beauty of Fractals. Images of Complex Dynamical Systems. Springer, Berlin