



On the application of polymer renormalization group theory to polymer-like microemulsions

Peter Schurtenberger, Carolina Cavaco

► To cite this version:

Peter Schurtenberger, Carolina Cavaco. On the application of polymer renormalization group theory to polymer-like microemulsions. Journal de Physique II, 1993, 3 (8), pp.1279-1288. 10.1051/jp2:1993198 . jpa-00247904

HAL Id: jpa-00247904

<https://hal.science/jpa-00247904>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

31.20 — 61.25H — 82.70

On the application of polymer renormalization group theory to polymer-like microemulsions

Peter Schurtenberger and Carolina Cavaco

Institut für Polymere, ETH Zentrum, CH-8092 Zürich, Switzerland

(Received 26 February 1993, accepted in final form 26 April 1993)

Abstract. — We report on the application of results from conformation space renormalization group theory for semi-dilute polymer solutions to « equilibrium polymers » such as worm-like micelles or microemulsions. We have tested this approach with data from an extensive static light scattering study of lecithin water-in-oil (w/o) microemulsions. We demonstrate that one can construct a universal curve $(M_w/RT)(\partial\Pi/\partial c)$ versus a reduced concentration $X \sim c/c^*$, where c^* is the overlap concentration, from the experimentally determined values of the osmotic compressibility if a power law of the form $M_w \sim c^a$ for the c -dependence of the average particle size is assumed. We show that one can thus obtain information from static light scattering experiments on the concentration dependence of both the micellar size distribution and the intermicellar interaction effects, i.e., on the weight average molecular weight $M_w(c)$ and the static structure factor $S(0, c)$.

Introduction.

The static and dynamic properties of « equilibrium polymers » (or « living polymers »), i.e., flexible linear macromolecules that can break and recombine, have recently been the subject of numerous theoretical and experimental studies. In particular surfactant systems in which giant worm-like micelles are formed have frequently been used as model systems. The analogy between flexible worm-like micelles and classical polymers has been postulated, and it has been suggested that micelles can entangle and form a transient network above a cross-over concentration c^* . Several reports have demonstrated that the results from static and dynamic light scattering and rheological measurements performed on viscoelastic surfactant solutions can in fact be successfully interpreted in terms of theories originally used to describe the behavior of semi-dilute polymer solutions [1-9].

However, while static properties of micellar solutions at $c > c^*$ such as the osmotic compressibility, $(\partial\Pi/\partial c)^{-1}$, or the static correlation length, ξ , directly obey the same simple scaling laws as do classical polymers, the dynamic behavior of « equilibrium polymers » can be very different. This is due to two fundamental differences between polymers and micelles :

(i) in micellar systems, the degree of polymerization (i.e., the average aggregation number, $\bar{N}$) is not constant but depends on surfactant concentration and temperature, and (ii) micelles are transient structures which can break and recombine and thus offer additional stress relaxation mechanisms. A theoretical model which describes the dynamic behavior of equilibrium polymers has been developed by Cates [10, 11]. It is based on the reptation theory for classical polymers, and takes into account the equilibrium molecular weight distribution and the finite life time of equilibrium polymers. The model predicts several dynamical regimes as a function of the relative contributions to stress relaxation due to diffusive polymer motion, reversible scission and recombination processes and chain length fluctuations, respectively. A number of simple scaling laws which describe the concentration dependence of dynamic quantities such as the polymer self diffusion coefficient, D_s , or the zero shear viscosity, η_s , emerge from this model, where the values of the scaling exponents strongly reflect the relative weight of the different contributions to stress relaxation. Several experimental studies with model systems such as ionic or nonionic aqueous micellar solutions or water-in-oil microemulsions have been performed, and the observed dependencies of D_s or η_s on surfactant concentration have been compared with the theoretical predictions for equilibrium polymers [1, 12-15].

However, the theory also predicts an explicit dependence of both quantities on $\bar{N}$. Since micelles have a concentration-dependent equilibrium molecular weight distribution $f(N)$ with an average $\bar{N}$ which is believed to follow a power law form $\bar{N} \sim c^\alpha$, this leads to an additional contribution to the c -dependence of D_s and η_s [1]. A quantitative interpretation of the experimental data would thus require an independent determination of α , which is difficult to achieve. Experimental techniques for molecular weight determinations in polymer solutions such as light scattering or osmotic pressure measurements always contain contributions both from the molecular weight distribution as well as from intermolecular interaction effects, i.e., from the static structure factor $S(0)$. In classical polymer solutions $\bar{N}$ can be obtained from a concentration dependence at low values of c , i.e., in the virial regime. However, unambiguous information on $\bar{N}$ is much more difficult to obtain for equilibrium polymers, since most systems form giant worm-like micelles even at concentrations close to the critical micelle concentration, the cmc. This makes a deconvolution of contributions from $f(N)$ and $S(0)$ very difficult, especially because simple virial expansions of $S(0)$ are not valid anymore at the values of c/c^* which can be achieved for most model systems investigated so far.

Here we now present an attempt to apply the results from conformation space renormalization group theory for semi-dilute polymer solutions to « equilibrium polymers » in order to obtain information on the concentration dependence of the equilibrium size distribution over a large range of surfactant concentrations. A universal scaling form of the scattering function $I(Q)$ was previously derived for classical polymers as a function of a reduced concentration $X = a(c/c^*) \sim cA_2 M_w$, where a is a constant, A_2 is the weight-average osmotic second virial coefficient and M_w is the weight-average molecular weight, respectively [16, 17]. The concentration dependence of measured quantities such as $(\partial \Pi / \partial c)^{-1}$ or ξ were compared with the theoretical predictions for polymers with different (but sufficiently high) values of molecular weight in good and marginal solvents. Very good agreement was found between the theory and the light scattering data for $10^{-2} < X < 10^2$.

We can thus try to use the fact that the dimensionless quantity $(M_w/RT)(\partial \Pi / \partial c)$ is a universal function of X . Knowing the correct scaling form for the molecular weight dependence of A_2 (or c^*), we can try to construct a « universal plot » $(M_w/RT)(\partial \Pi / \partial c)$ versus X for equilibrium polymers, where $M_w \sim c^\alpha$ is now a concentration dependent quantity. A comparison of the experimentally determined c -dependence of $(\partial \Pi / \partial c)$ with the renormaliza-

tion theory predictions should then allow for a quite accurate determination of α , provided that the analogy between classical polymers and equilibrium polymers holds.

We have tested this approach with data from an extensive light scattering study of lecithin water-in-oil (w/o) microemulsions. Lecithin w/o microemulsions represent a unique system which shows a characteristic sphere-to-rod transition normally observed in aqueous solutions only. On the basis of dynamic (QLS) and static (SLS) light scattering we were able to show that lecithin/cyclohexane reverse micellar solutions exhibit two characteristic concentration dependent regimes. At low values of the molar ratio of water to surfactant, w_o , the micelles are small and the solutions have static and dynamic properties which are typical for classical micellar or colloidal solutions. At high values of w_o , the micellar size can be extremely large, and the micelles have polymer-like properties. Using a combination of light scattering and small angle neutron scattering (SANS), we were able to directly confirm the existing structural model and verify the postulated analogy between the structural properties of polymer chains and lecithin reverse micelles [15, 18-20].

Since the system is oil-continuous and no complicating effects arise due to additional contributions from electrostatic interactions or salt effects, reverse micellar solutions of lecithin in organic solvents such as isooctane or cyclohexane serve as good model systems for structural and dynamic studies of « equilibrium polymer » solutions. However, while a number of interesting and quite novel results for the dynamic properties have already been reported, a quantitative analysis in terms of the theoretical model by Cates *et al.* was rather ambiguous due to the missing information on the concentration dependence of the equilibrium size distribution [13-15]. It is the purpose of this contribution to show that this can now be achieved from an application of polymer renormalization group theory results to the experimentally determined concentration dependence of $(\partial I/\partial c)^{-1}$ in lecithin/cyclohexane/water solutions.

Materials and methods.

Soybean lecithin was obtained from Lucas Meyer (Epikuron 200) and used without further purification. Cyclohexane (spectroscopic grade) was purchased from Fluka. Samples were prepared as described previously [15, 19]. Static light scattering measurements were made with a Malvern 4700 PS/MW spectrometer, equipped with an argon ion laser (Coherent, Innova 200-10, $\lambda_0 = 488$ nm) and a computer controlled and stepping motor driven variable angle detection system. Measurements were usually performed at a temperature of 25.0 ± 0.1 °C. Approximately 1 ml of solution was transferred into the cylindrical scattering cell (10 mm inner diameter). The scattering cell was then sealed and centrifuged between 20 and 420 minutes at approximately 5 000 g and 25 °C in order to remove dust particles from the scattering volume.

Experiments were generally performed at 13 different angles ($30^\circ \leq \theta \leq 150^\circ$), and 30 to 100 individual measurements were taken and averaged for each angle. The data was then corrected for background (cell and solvent) scattering and converted into absolute scattering intensities $\Delta R(0)$ (i.e. « excess Rayleigh ratios ») using toluene as a reference standard. The excess Rayleigh ratio of the sample was calculated using

$$\Delta R(\theta) = \frac{\Delta \langle I(\theta) \rangle}{\langle I_{\text{ref}}(\theta) \rangle} \cdot R_{\text{ref}}(\theta) \cdot \left(\frac{n}{n_{\text{ref}}} \right)^2, \quad (1)$$

where $\Delta \langle I(\theta) \rangle$ and $\langle I_{\text{ref}}(\theta) \rangle$ are the average excess scattering intensity of the solution and the average scattering intensity of the reference solvent toluene, $R_{\text{ref}}(\theta) = 39.6 \times 10^{-4} \text{ m}^{-1}$ is the Rayleigh ratio of toluene, and n and n_{ref} are the index of refraction of the solution and the reference solvent, respectively [21]. Plots of $Kc/\Delta R(\theta)$ versus $Q^2/3$ were extrapolated to

$Q = 0$ to give intercepts $Kc/\Delta R(0)$, where $K = 4 \pi^2 n^2 (dn/dc)^2 / (N_A \cdot \lambda_0^4)$, dn/dc is the refractive index increment, $|Q| = (4 \pi n / \lambda_0) \sin(\theta/2)$ is the scattering vector, and c is the concentration of surfactant plus water, respectively. Values of dn/dc for soybean lecithin in cyclohexane were measured as a function of w_0 with a modified Brice-Phoenix differential refractometer with a resolution better than $\Delta n = 2 \times 10^{-5}$.

Results and discussion.

The results from systematic static light scattering measurements of lecithin/cyclohexane w/o microemulsion solutions are summarized in figure 1, where $\Delta R(0)/Kc$ is plotted as a function of the concentration of the dispersed phase (surfactant plus water) for different values of w_0 . In figure 1 we observe two characteristic regimes which exhibit a very different dependence on c and w_0 . At low concentrations $c < 10$ mg/ml, the dramatic increase of $\Delta R(0)/Kc$ with increasing values of w_0 primarily reflects the pronounced water-induced growth from small microemulsion particles at $w_0 = 2.0$ to giant worm-like structures at $w_0 \geq 6$. We previously demonstrated this water-induced sphere-to-flexible coil transition with a combination of light scattering and small angle neutron scattering (SANS) at low surfactant concentrations, and were able to verify the locally cylindrical structure of these reverse micelles and to estimate their flexibility (the persistence length, ℓ_p) and overall dimensions (contour length, L) [18, 19]. In addition to the clear manifestation of the water-induced micellar growth for $c < 10$ mg/ml, we can observe an increase of $\Delta R(0)/Kc$ with increasing c , indicating a c -dependence of the average molecular weight which is particularly visible at low values of w_0 , i.e., under conditions where the resulting aggregates are small and

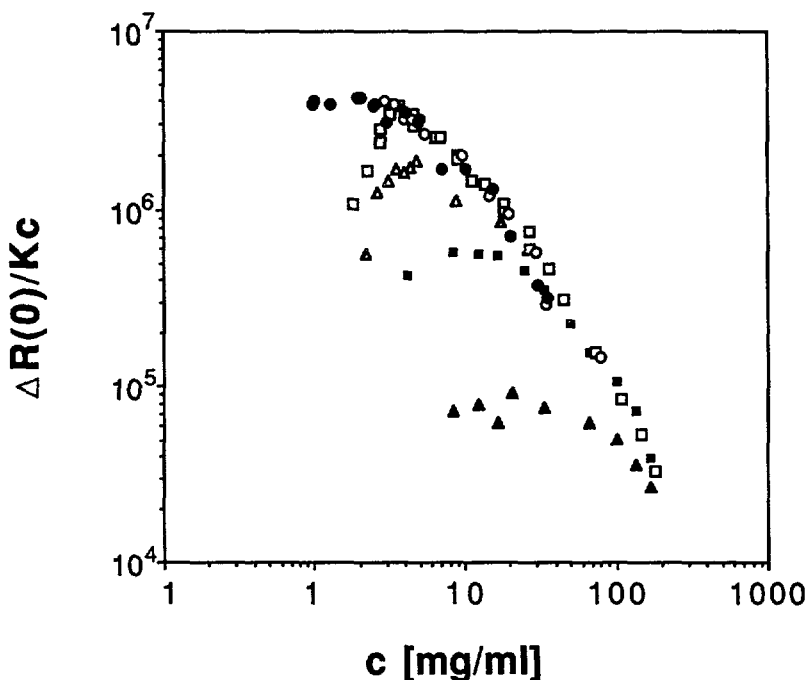


Fig. 1. — $\Delta R(0)/Kc$ as a function of the concentration c of the dispersed phase for lecithin/cyclohexane w/o microemulsions at different values of w_0 : ($\blacktriangle$): $w_0 = 2.0$; ($\blacksquare$): $w_0 = 4.0$; ($\triangle$): $w_0 = 6.0$; ($\square$): $w_0 = 8.0$; ($\circ$): $w_0 = 12.0$; ($\bullet$): $w_0 = 14.0$.

$c \ll c^*$. At $w_0 \geq 10$, the microemulsion particles are extremely large even at the lowest values of c investigated, c^* is thus shifted to quite low values and the c -dependence of M is masked by the strong intermicellar interaction effects.

At higher concentrations, $\Delta R(0)/Kc$ becomes independent of w_0 and decreases with increasing c . The c -dependence can now be described by a power law of the form $\Delta R(0)/Kc \sim \Phi^{-1}$, where $x = 1.30 \pm 0.05$. Such a power law dependence for $\Delta R(0)/Kc$ is in quite good agreement with the proposed analogy to classical polymer solutions, for which the osmotic compressibility should become independent of M and follow a scaling law of the form [22, 23]

$$\left(\frac{\partial \Pi}{\partial c} \right)^{-1} = \frac{1}{N_A k_B T} \frac{\Delta R(0)}{Kc} \sim c^{-1.31}, \quad (2)$$

for $c \gg c^*$. From figure 1 we see that the concentration range where a power law dependence of $\Delta R(0)/Kc$ can be observed extends to much lower values of c for high values of w_0 . This is in qualitative agreement with the dependence of c^* on M , which for flexible chains can be estimated using [22, 24]

$$c^* \approx \frac{3M}{4\pi N_A R_g^3}. \quad (3)$$

Due to the strong water-induced growth of the microemulsion particle size we can thus expect that c^* decreases with increasing w_0 , in agreement with the experimental results shown in figure 1.

The basis for a quantitative interpretation of the data is the connection between the scattered intensity and the osmotic compressibility given in equation (2). In the limit of $Q \rightarrow 0$, $(\partial \Pi / \partial c)^{-1}$ is related to the static structure factor $S(Q)$ by the relation [25]:

$$S(0) = \frac{N_A}{M} k_B T \left(\frac{\partial \Pi}{\partial c} \right)^{-1} \quad (4)$$

We can define an apparent molecular weight M_{app} through:

$$\frac{\Delta R(0)}{Kc} = M_w S(0) = M_{app}. \quad (5)$$

For low concentrations we can use virial expansions of the form [25]:

$$S(0) = 1 - 2 A_2 M_w c + \dots \quad (6)$$

where A_2 is the second virial coefficient. For flexible coils, quite reliable expressions exist for A_2 , and we can use for example [26]:

$$A_2 \approx 4 \pi^{3/2} N_A \frac{\langle R_g^2 \rangle^{3/2}}{M_w^2} \Psi, \quad (7)$$

where R_g is the radius of gyration of the polymer coil and Ψ is the degree of interpenetration in dilute solution, i.e., describes the influence of the solvent quality.

However, virial expansions can be used for $c/c^* \ll 1$ only, which represents a serious limitation in our system. The lecithin microemulsion can not be diluted to too low values of c , since the particle composition would otherwise change due to the low but finite solubility of the surfactant monomers and water in the organic solvent. In particular for high values of

w_0 and correspondingly large values of M and R_g we can thus not perform experiments under conditions $c \ll c^*$ which would be required for the use of equation (6). In a next level of approximation we could try to calculate $S(0)$ by using simple liquid theories. In particular the semi-empirical extension of the Percus-Yevick theory derived by Carnahan and Starling [27] provides us with a very accurate analytical expression for the osmotic pressure of a hard sphere suspension as a function of the hard sphere volume fraction Φ , which has frequently been used to analyze interaction effects in colloidal suspensions and microemulsions [28]. We could approximate polymer coils with hard spheres of radius $R \sim R_g$, and Φ could then be replaced by c/c^* , since c^* corresponds to the « internal » concentration of the spheres. While this provides us with an expression for $S(0)$ which is valid to much higher concentrations than a simple virial expression, the hard sphere model will still break down for $c \sim c^*$, and in particular is not capable to reproduce the scaling law for $(\partial \Pi / \partial c)^{-1}$ at $c \gg c^*$.

An estimate of the concentration dependence of the microemulsion particle size distribution based on a virial expansion (Eq. (6)) or on simple liquid theories and the experimentally determined values of $\Delta R(0)/Kc$ shown in figure 1 is thus severely limited. However, for flexible chains an expression for $S(0)$ has recently been derived by Ohta and Oono on the basis of conformation space renormalization group theory [16]:

$$S(0)^{-1} = 1 + \frac{1}{8} \left[9X - 2 + \frac{2 \ln(1+X)}{X} \right] \exp \left\{ \frac{1}{4} \left[\frac{1}{X} + \left(1 - \frac{1}{X^2} \right) \ln(1+X) \right] \right\}, \quad (8)$$

where $X \sim c/c^*$ is related to the second virial coefficient through

$$X = \frac{A_2 c M_w}{\frac{9}{16} - \frac{\ln \frac{M_w}{M_n}}{8}} \quad (9)$$

We can now try to analyze the experimentally determined values of $\Delta R(0)/Kc$ as a function of X using equations (5) and (8), i.e., attempt a fit of $\Delta R(0)/Kc = M_w S(0, X)$. In contrast to classical polymer solutions there are additional difficulties in the application of equation (8) to our microemulsion system, since M_w and A_2 can not be determined directly and will be dependent on c . We thus have to make assumptions on the exact form of the c -dependence of M_w and A_2 . Based on multiple chemical equilibrium models or scaling arguments, the average molecular weight in a micellar solution is supposed to increase with increasing surfactant concentration with a power law of the form $M_w \sim c^\alpha$. For mean field models, α varies between $\alpha = 1/2$ based either on law of mass-action or Flory-Huggins lattice model calculations, and $\alpha \approx 0.6$ when using a scaling theory approach for semi-dilute solutions [1]. These models predict an exponential size distribution of the form $n(M) \sim \exp(-M/M_w)$, which results in $M_w/M_n \approx 2$. We can thus use an expression of the form

$$M_w = B_1 c^\alpha \quad (10)$$

where B_1 is a constant, in equations (8) and (9) in order to describe the additional c -dependence of the size distribution in equilibrium polymers at sufficiently high values of c ($c \gg \text{cmc}$).

Based on equation (10) we can now try to take into account the c -dependent equilibrium size distribution in A_2 . If excluded volume interactions represent the dominating contribution to the second virial coefficient, $A_2 \sim \langle R_g^2 \rangle^{3/2} / M_w^2$ (see Eq. (7)). For polymers, R_g scales with M according to $R_g \sim M^\nu$, where the exponent ν varies between $1/2$ for theta solvents and 0.588 for good solvents [17, 22, 26]. We can thus try to use an expression of the form $A_2 = B_2 M_w^{3\nu-2} =$

$B_2 B_1^{3\nu-2} c^{\alpha(3\nu-2)}$, where B_2 is a constant which links the second virial coefficient to R_g and M_w . Under the assumption of $M_w/M_n \approx 2$ [29] and using equations (9) and (10), we obtain the following expression for X

$$X = 2.10 B_1^{(3\nu-1)} B_2 c^{[\alpha(3\nu-1)+1]} \quad (11)$$

Together with equations (5), (8) and (10) we then obtain

$$\frac{Kc}{\Delta R(0)} = \frac{1}{B_1 c^\alpha} \left[1 + \frac{1}{8} \left[9X - 2 + \frac{2 \ln(1+X)}{X} \right] \exp \left\{ \frac{1}{4} \left[\frac{1}{X} + \left(1 - \frac{1}{X^2} \right) \ln(1+X) \right] \right\} \right] \quad (12)$$

where X is given by equation (11). We can now try to fit the experimentally determined intensity data as a function of c for the different values of w_o and thus deduce the concentration dependence of the micellar size distribution in a self consistent way by making an analogy to classical polymer solutions.

However, fitting equation (12) to the experimental data requires the determination of 4 independent parameters with a highly non-linear fit function. Moreover, we can expect that the scaling relations which represent the basis of equation (12) hold for sufficiently large polymers only. We have thus started our analysis by performing a grid search procedure keeping the excluded volume exponent fixed at the good solvent limit $\nu = 0.588$ and, for $w_o \leq 4.0$, by using the data for sufficiently high values of c only. After a first set of iterations which yielded guesses for B_1 , B_2 and α , the constraints were released and a full set of parameters were determined from the data for each value of w_o . The best fit values of $\alpha = 1.2 \pm 0.3$, $\nu = 0.57 \pm 0.03$ and $B_2 = (0.8 \pm 0.3) \times 10^{-6} \text{ cm}^3 \text{ mol}^{(3\nu-1)} \text{ g}^{-3\nu}$ thus obtained were independent of w_o , whereas the values of B_1 summarized in table I depend strongly upon w_o and reflect the pronounced water-induced micellar growth. It is interesting to note that the w_o -dependence of B_1 appears to level off at high w_o , which is in agreement with previous dynamic and static light scattering studies on the w_o -dependence of the micellar size at low concentrations [18]. These measurements indicated that the size of the microemulsion particles increases monotonically with increasing w_o and reaches a plateau after $w_o \approx 12$.

Having these parameters, we can now calculate X from equation (11) and $S(0)^{-1}$ using $S(0)^{-1} = [Kc/\Delta R(0)] c^{1.2} B_1$ for each value of w_o and c investigated in our light scattering study. The resulting data points are shown in figure 2, together with the theoretical curve for

Table I. — w_o -dependence of the constant term B_1 used in the relation between surfactant concentration and average molecular weight ($M_w = B_1 c^\alpha$) for lecithin/cyclohexane w/o microemulsions.

w_o	B_1 [g ^(1-α) /mol ^(1-α)]
2.0	$(2.7 \pm 0.6) \times 10^3$
4.0	$(4.5 \pm 0.8) \times 10^4$
6.0	$(6.0 \pm 0.5) \times 10^5$
8.0	$(1.6 \pm 0.3) \times 10^6$
12.0	$(7.6 \pm 0.5) \times 10^6$
14.0	$(1.0 \pm 0.1) \times 10^7$

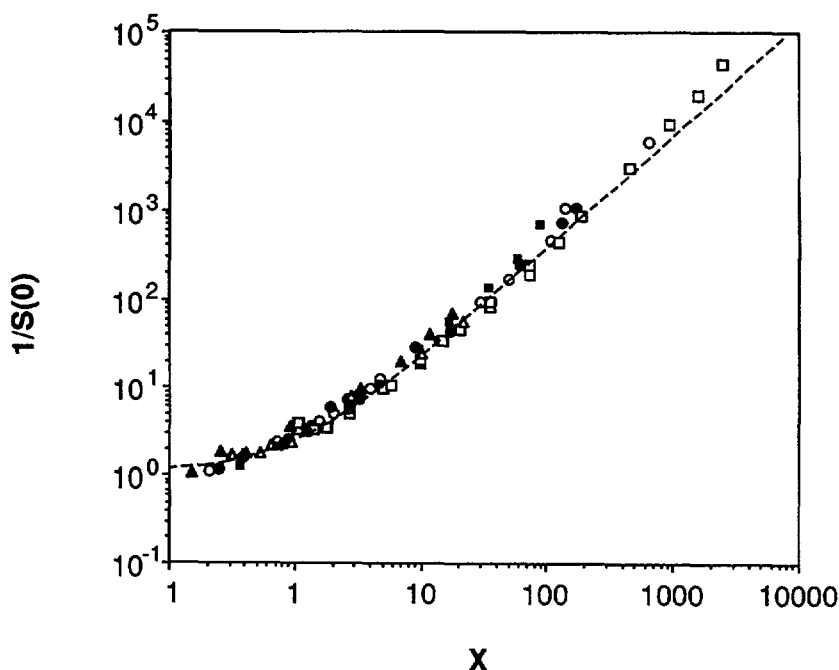


Fig. 2. — $S(0)^{-1}$ ($= [Kc/\Delta R(0)] c^{1/2} B_1$) as a function of reduced concentration X (Eq. (12)) for lecithin/cyclohexane w/o microemulsions at different values of w_0 : ($\blacktriangle$): $w_0 = 2.0$; ($\blacksquare$): $w_0 = 4.0$; ($\triangle$): $w_0 = 6.0$; ($\square$): $w_0 = 8.0$; ($\circ$): $w_0 = 12.0$; ($\bullet$): $w_0 = 14.0$. Also shown in the theoretical curve $S(0)^{-1}$ vs. X for classical polymers from renormalization group theory (Eq. (8)) as the dashed line.

polymer solutions based on renormalization group theory (Eq. (8)). We see from figure 2 that we can successfully construct a « universal » master curve with the data from figure 1, despite the fact that the raw data from the static light scattering experiments exhibits a very pronounced w_0 and c dependence. Moreover, the agreement between polymer theory and the microemulsion data is very good, thus supporting our attempt to apply polymer renormalization group theory to « equilibrium polymers » such as worm-like micelles.

When looking at the values of α and ν obtained from our data analysis, we see that $\nu = 0.57$ is in quite good agreement with polymer theory, whereas $\alpha = 1.2$ appears to be very large when compared to the theoretical predictions from mean field models and scaling arguments. The particle sizes for $w_0 = 2.0$ are probably too small for an unambiguous application of equation (12), and thus for a conclusive estimate of α . However, for $w_0 \geq 6.0$ recent neutron and light scattering experiments [30] clearly show the close analogy between the scattering function $I(Q)$ of lecithin reverse micelles and flexible polymer coils and demonstrate that $L \gg \ell_p$ for all concentrations investigated. Moreover, preliminary results from Kerr effect measurements [31] with lecithin/cyclohexane w/o microemulsions also indicate a power law dependence of the particle size on concentration with an exponent which is of the same order as obtained in the present light scattering study. It is thus clear that additional theoretical work on the aggregation processes in lecithin w/o microemulsions is required. Furthermore, an extension of our study to a two component aqueous micellar system, where the previously published experimental data was in agreement with the currently existing theories of micelle formation, would be very helpful. Despite the open questions, our results clearly indicate that a direct application of the growth laws proposed for micellar systems to strongly interacting giant micelles in semi-dilute solutions should be done with caution.

Conclusions.

Our results presented above show that we can directly apply the results from conformation space renormalization group theory for semi-dilute polymer solutions to « equilibrium polymers » such as worm-like micelles or microemulsions if we take into account the fact that their size distribution is concentration dependent. In particular we have demonstrated that we can construct a universal curve $(M_w/RT)(\partial\Pi/\partial c)$ versus $X = a(c/c^*)$ from the experimentally determined values of the osmotic compressibility measured over a wide range of microemulsion composition if we assume a power law of the form $M_w \sim c^\alpha$ for the c -dependence of the average particle size. Based on the analogy between giant worm-like micelles or microemulsion particles and classical polymers, it is thus possible to go well beyond a simple confirmation of scaling laws for $(\partial\Pi/\partial c)^{-1}$ or ξ at $c > c^*$. We can for example obtain information from static light scattering experiments on both the micellar size distribution and the intermicellar interaction effects, i.e., on M_w and $S(0)$. It will be interesting to investigate whether we can extend this approach to an interpretation of the full scattering curve $I(Q)$ obtained by light and neutron scattering as a function of reduced concentration X in terms of the universal scaling function derived for polymers in order to get detailed structural information.

Acknowledgements.

This work was supported in part by the Portuguese National Fund for Technological and Scientific Research through the Grant BD/1256/91-IC. We gratefully acknowledge helpful discussions with Professor H. C. Oettinger.

References

- [1] Cates M. E. and Candau S. J., *J. Phys. . Condens. Matter* **2** (1990) 6869 ; and references therein.
- [2] Hoffmann H. and Rehage H., *Surf. Sci. Ser.* **22** (1987) 209.
- [3] Rehage H. and Hoffmann H., *Mol. Phys.* **74** (1991) 933.
- [4] Candau S. J., Hirsch E. and Zana R., *J. Colloid Interface Sci.* **105** (1985) 521.
- [5] Candau S. J., Hirsch E., Zana R. and Adam M., *J. Colloid Interface Sci.* **122** (1988) 430.
- [6] Appell J. and Porte G., *J. Phys. Lett. France* **44** (1983) L-689.
- [7] Marignan J., Appell J., Bassereau P., Porte G. and May R. P., *J. Phys. France* **50** (1989) 3553.
- [8] Appell J., Porte G., Khatory A., Kern F. and Candau S. J., *J. Phys. II France* **2** (1992) 1045.
- [9] Wu X.-I., Yeung C., Kim M. W., Huang J. S. and Ou-Yang D., *Phys. Rev. Lett.* **68** (1992) 1426.
- [10] Cates M. E., *Macromolecules* **20** (1987) 2289.
- [11] Cates M. E., *J. Phys. France* **49** (1988) 1593.
- [12] Messenger R., Ott A., Chatenay D., Urbach W. and Langevin D., *Phys. Rev. Lett.* **60** (1988) 1410.
- [13] Ott A., Urbach W., Langevin D., Schurtenberger P., Scartazzini R. and Luisi P. L., *J. Phys. . Condens. Matter* **2** (1990) 5907.
- [14] Schurtenberger P., Scartazzini R. and Luisi P. L., *Rheol. Acta* **28** (1989) 372.
- [15] Schurtenberger P., Scartazzini R., Magid L. J., Leser M. E. and Luisi P. L., *J. Phys. Chem.* **94** (1990) 3695.
- [16] Ohta T. and Oono Y., *Phys. Lett.* **89A** (1982) 460.
- [17] Nakanishi A. and Ohta T., *J. Phys. A* **18** (1985) 127.
- [18] Schurtenberger P., Magid L. J., Lindner P. and Luisi P. L., *Prog. Colloid Polym. Sci.* **89** (1992) 274.
- [19] Schurtenberger P., Magid L. J., King S. M. and Lindner P., *J. Phys. Chem.* **95** (1991) 4173.
- [20] Schurtenberger P. and Cavaco C., manuscript in preparation.

- [21] Schurtenberger P. and Augusteyn R. C., *Biopolymers* **31** (1991) 1229.
- [22] De Gennes P. G., *Scaling Concepts in Polymer Physics* (Cornell Univ. Press : Ithaca, N.Y., 1979).
- [23] Daoud M., Cotton J. P., Farnoux B., Jannink G., Sarma G., Benoit H., Duplessix R., Picot C. and de Gennes P. G., *Macromolecules* **8** (1975) 804.
- [24] Ying Q. and Chu B., *Macromolecules* **20** (1987) 362.
- [25] Goodstein D. L., *States of Matter* (New York : Dover, 1985).
- [26] Yamakawa H., *Modern Theory of Polymer Solutions* (New York, Harper & Row, 1971).
- [27] Carnahan N. F. and Starling K. E., *J. Chem. Phys.* **51** (1969) 635.
- [28] Agterof W. G. M., van Zomeren J. A. J. and Vrij A., *Chem. Phys. Lett.* **43** (1976) 363.
- [29] It is important to point out that although we have chosen an explicit value for M_w/M_n , it enters only as a (constant) prefactor in equation (11). While the choice of M_w/M_n influences slightly the resulting absolute values of B_1 and B_2 , it has no detectable influence on α .
- [30] Schurtenberger P., Cavaco C., Lindner P. and Pedersen J. S., to be published.
- [31] Cavaco C., Schurtenberger P. and Koper G., to be published.