Viscosity of Wormlike Micelles: Determination of the End Cap Energy and Persistence Length

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We propose a theory for the zero-shear viscosity of a dilute solution of wormlike micelles, with a length distribution as derived by Israelachvili, Mitchell, and Ninham. An analytical approach using Bohdanecký's approximation to the full Yamakawa−Fujii−Yoshizaki description (YFY) for the viscosity of wormlike objects is combined with a numerical integration of the YFY equations. In principle, this provides a convenient means of extracting the growth parameters, dimensions, and persistence length of linear micelles from measurements of the viscosity as a function of the surfactant concentration.

1. Introduction

The interpretation of viscosity measurements for linear micelles is a long-standing issue.[1−8] None of the reported studies, however, simultaneously account for their rather broad length distribution and their semiflexibility. This is probably the reason why such a simple technique as viscometry has not been fully exploited in the characterization of dilute solutions of wormlike micelles. The problem is becoming urgent, especially as there is no catalog of growth parameters, diameters, and persistence lengths for various micellar systems. This knowledge is essential in order to test theories on self-assembly quantitatively. We have published theories on sedimentation techniques for the same reason.[9,10]

This paper is organized as follows: Section 2 describes a tractable analytical calculation based on Bohdanecký's interpolation formula.[11] In section 3, a numerical refinement to this is obtained so that we can analyze the experimental data by Kushner et al.[12] in section 4. This yields values for the persistence length and the end cap energy and allows us to make a comparison with theoretical work on the ionic-strength dependence of the latter.

2. Analytical Approximation

We here assume that, in an experiment, the viscosity extrapolated down to zero rate of shear is an equilibrium quantity; i.e., it is independent of micellar scission and recombination rates and the amphiphilar chemical potential is constant. If this supposition turns out to be incorrect, this will show up as an anomalous concentration dependence of the viscosity. Next, we suppose the concentration of single amphiphiles to be invariant beyond the critical micellar concentration (cmc).[13] A complete theory for the viscosity of semiflexible micelles is difficult

because there is a variety of end effects that are not known precisely. We will mention all end effects in our analysis below. In addition, a bare numerical computation is basically out of the question in view of the large number of independent variables in the problem. We need a reliable expression we can fit to experimental data. Hence, our strategy will be to develop a convenient analytical approximation first. This will enable us to compute a precise numerical correction which is feasible to couch in terms of the experimental variables. In the end, we obtain an essentially rigorous expression for the viscosity as a function of the surfactant concentration.

The distribution of amphiphiles is given by[14−16]

$$X(s) = s^n e^{-\lambda s - K} \tag{2.1}$$

for long enough micelles; i.e., the number of amphiphiles within a linear micelle $s \geq s_0$, where s_0 is some minimum aggregation number. Here, $X(s)$ is the mole fraction of amphiphiles in the state of aggregation indexed s, n is related to the number of degrees of freedom an amphiphile loses upon aggregation, and K is the end cap energy in units of $k_B T$. In the classical picture of micellization in which the mixing is ideal,[14] one has $n = 1$ but it has been argued that n may take on other values.[15,16] The total mole fraction of amphiphiles X determines the constant λ

$$X \equiv \int_{s_0}^{\infty} ds \, X(s) \tag{2.2}$$

Since the distribution $X(s)$ is reasonably sharp, we shall use the Laplace method to approximate eq 2.2 and a similar expression for the viscosity below, so as to develop a consistent analytical scheme. Hence, upon replacing eq 2.1 by an effective Gaussian, we get

$$\lambda = \lambda(X) \simeq (2\pi)^{1/(2n+2)} n^{(2n+1)/(2n+2)} (X e^{n+K})^{-1/(n+1)} \tag{2.3}$$

In the zero-shear limit we calculate the viscosity η of a dilute solution of linear micelles by summing over the respective contributions arising from the individual micelles weighted by the equilibrium distribution $X(s)$:

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$$H \equiv \frac{\eta}{\eta_{cmc}} - 1 = \int_{s_c}^{\infty} ds \, [\eta]_s \, (C - C_{cmc}) \quad (2.4)$$

where $[\eta]_s$ is the intrinsic viscosity of those micelles containing s amphiphiles and the concentration is defined with respect to the cmc: $C - C_{cmc} \equiv C_0 M_1 (X(s) - X_{cmc})$, C_0 being the molar density of solvent molecules and M_1 the molar mass of the amphiphile. Here, we consider the linear micelles to be immersed in an effective medium of viscosity η_{cmc} which consists of solvent molecules and free amphiphiles at the fixed total mole fraction X_{cmc}. The lower integration boundary has been set equal to s_c (s_c is the number of amphiphiles residing in both end caps), as spherical micelles are the preferred form just above the cmc and because s_c is a lower bound to the unknown s_0.

Next, the intrinsic viscosity $[\eta]$ of a wormlike polymer chain of contour length $\angle$, persistence length P, and diameter $\oslash$ has been calculated by Yamakawa, Fujii, and Yoshizaki (YFY).[17-19] In terms of the reduced variables $D \equiv \oslash/2P$ and $L \equiv \angle/2P$, one has in the semiflexible limit

$$[\eta] = \frac{\Phi_\infty}{M} (2P\angle)^{3/2} \left(1 - \sum_{j=1}^{4} C_j L^{-j/2}\right)^{-1} \quad \text{for} \quad L \geq 2.278 \quad (2.5a)$$

with

$$c_j = \sum_{k=0}^{2} \alpha_{jk} D^k + \sum_{k=0}^{1} \beta_{jk} D^{2k} \ln D$$

The coefficients α_{jk} and β_{jk} have been tabulated separately for $D \leq 0.1$ and $0.1 \leq D \leq 0.2$ in Tables I and II of ref 19. In the other regime we have

$$[\eta] = [\eta]_{rod} f(L) \quad \text{for} \quad L < 2.278 \quad (2.5b)$$

where $f(L)$ is a fifth-degree polynomial given by eqs 32 and 33 of ref 19 and $[\eta]_{rod}$ is the intrinsic viscosity of the chain if it were infinitely stiff

$$[\eta]_{rod} = \frac{\pi N_A \angle^3}{24M} F_2(L/D) \quad (2.5c)$$

The function $F_2(L/D)$ for cylinders with hemispherical caps can be found by setting the eccentricity ϵ equal to 1 in eqs 27-30 of ref 19. Yamakawa and Yoshizaki showed that the viscosity is independent of the exact form of the end caps for $L/D \geq 4$, within reasonable bounds.[19] In the above expressions $\Phi_\infty = 2.87 \times 10^{23}$ mol^{-1} is the Flory viscosity factor and N_A is Avogadro's number. In our case, the contour length $\angle$ and the molar mass M are now the following functions of s

$$\angle = \frac{1}{3}(1 + 2ss_c^{-1})\oslash \quad (2.6a)$$

$$M = M_1 s \quad (2.6b)$$

if we suppose the semiflexible micelles have hemispherical caps of the same diameter $\oslash$ as that of the cylindrical body.

Clearly a full analytical treatment of eqs 2.1-2.6 is impractical, but fortunately, Bushin et al.[20] and, in particular, Bohdanecký[11] have provided a very useful

approximation to eqs 2.5a-c of the form

$$[\eta] \simeq \frac{\Phi_\infty \angle^3}{M(A + BL^{1/2})^3} \quad (2.7)$$

Here, A and B are functions of D. The use of eq 2.7 is restricted in view of the bounds on the reduced diameter and length. The accuracy and range of Bohdanecký's original interpolation formulas (eqs 8 and 9 in ref 11) proved insufficient for our purposes, so two fourth-order polynomials are fitted to Bohdanecký's Table I for $0.01 \leq D \leq 0.2$

$$A = 1.7341 - 22.748D + 296.65D^2 - 1898.0D^3 + 4183.7D^4 \quad (2.8a)$$

$$B = 1.0721 - 0.7314D - 6.9602D^2 + 106.54D^3 - 309.82D^4 \quad (2.8b)$$

All nonlinear fits in this paper have been performed with a Levenberg–Marquardt routine.[21] Neglecting end effects in the expression for $\angle$ and M (i.e. terms independent of s) for long enough micelles and combining eqs 2.1, 2.4, and 2.7, we get

$$H \simeq \Phi_\infty C_0 (2\oslash/3s_c)^3 e^{-K} \int_{s_c}^{\infty} ds \frac{s^{n+2} e^{-\lambda s}}{(A + B(2D/3s_c)^{1/2} s^{1/2})^3} \quad (2.9)$$

As we have pointed out above, we know that the integrand is reasonably sharply peaked and that its maximum value s_m lies well within the upper and lower limits of validity of eq 2.7, depending on D. The variance is not very small, but any error incurred will be compensated in part by our earlier use of the Laplace method. The extension of the integration interval to the whole s domain is thus allowed within an approximation correct to the leading order.

The integral in eq 2.9 can now be computed by the Laplace method. After the substitutions $s \equiv 3s_c A^2 t/2DB^2$ and $\lambda s \equiv \mu t$ it becomes to the leading order

$$I \simeq A^{-3}(3A^2 s_c/2B^2 D)^{n+3} \int_{-\infty}^{\infty} dt \, e^{f(t)} \quad (2.10)$$

where

$$f(t) \equiv (n+2) \ln t - \mu t - 3 \ln(1 + t^{1/2}) \quad (2.11)$$

The location t_m of the maximum of f is given by

$$\mu = \frac{1}{t_m}\left[n + 2 - \frac{3}{2(1 + t_m^{-1/2})}\right] \quad (2.12)$$

Since the term in square brackets is a monotone decreasing function of t_m, eq 2.12 defines t_m uniquely. This third-order algebraic equation is tedious to solve exactly, since the corresponding discriminant may be positive or negative. Nevertheless, considering the forms eq 2.12 adopts in the limits $t \to 0$ and $t \to \infty$, we obtain a zero-order guess by arithmetic interpolation

$$t_0 = \frac{1}{\mu}(n + (5/4)) \quad (2.13)$$

which is exact for $t \to 0$, $t = 1$, and $t \to \infty$. A very good approximation to the true solution is now obtained when

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t_0 is substituted in the term in square brackets in eq 2.12, which yields

$$t_{\mathrm{m}} \simeq \frac{1}{\mu}\left(n + 2 - \frac{3}{2(1 + ((n + (5/4))/\mu)^{-1/2})}\right) \quad (2.14)$$

Our asymptotic evaluation thus yields

$$I \simeq A^{-3}(3A^2 s_c/2B^2 D)^{n+3}\mathrm{e}^{f(t_{\mathrm{m}})}(-2\pi/f'(t_{\mathrm{m}}))^{1/2} \quad (2.15)$$

where f' is the second derivative of f with respect to t

$$f'(t_{\mathrm{m}}) = \frac{1}{t_{\mathrm{m}}^2}\left(-n - 2 + \frac{3(1 + (1/2)t_{\mathrm{m}}^{-1/2})}{(1 + t_{\mathrm{m}}^{-1/2})^2}\right) \quad (2.16)$$

Hence, from eq 2.9 one obtains for the relative viscosity increment the following analytical expression

$$H_{\mathrm{anal}} \simeq \Phi_\infty C_0(2\square/3s_c)^3 \mathrm{e}^{-K} A^{-3}(3A^2 s_c/2B^2 D)^{n+3} \times$$
$$\mathrm{e}^{f(t_{\mathrm{m}})}(-2\pi/f'(t_{\mathrm{m}}))^{1/2} \quad (2.17)$$

Note that the dependence on the total mole fraction $\Delta X \equiv X - X_{\mathrm{cmc}}$ enters only via t_{m}. Moreover, all end effects have been simply deleted.
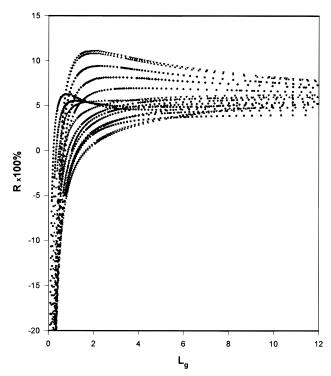
3. Numerical Analysis ($n = 1$)

In what follows n is set equal to unity (i.e. we consider ideal mixing only).[14] Other choices for n are briefly discussed at the end of this section. To improve the accuracy of the analytical approximation $H_{\mathrm{anal}} = H_{\mathrm{anal}}(\Delta X)$ derived in the previous section, we performed full numerical integrations of the YFY formulas. All integrations have been carried out on the interval from s_c ($= O(10^2)$) to infinity effectively. Our results are not sensitive to the precise value of the lower integration limit; s_c is set equal to 57, as in ref 4. To ensure convergence, the interval is split into two parts: (I) (s_c, $s_g + 4\sigma$) and (II) ($s_g + 4\sigma$, $s_g + 40\sigma$). We know that the micellar distribution $X(s)$ (eq 2.1) approximates a Gaussian with mean $s_g = n/\lambda$ and standard deviation $\sigma = n^{1/2}/\lambda$. On each interval a Romberg integration procedure (with an extended trapezoidal rule)[21] is used with a fixed error of 10^{-6}.

First, the relation between X_{num} and some convenient λ for a given K and $n = 1$ (as expressed only approximately in eq 2.3) has to be tabulated. Values of λ are chosen such that, after the numerical integration, all values of the total mole fraction X lie roughly between 10^{-4} and 10^{-3}, as would be the case in an experiment. The contribution from the second interval is typically 10% of the total sum for all integrations performed. We have checked that extension of the second interval to include higher values of s makes no difference in the results.

The relative deviation $R \equiv (H_{\mathrm{anal}} - H_{\mathrm{num}})/H_{\mathrm{num}}$ between the analytical result $H_{\mathrm{anal}}(X)$ and the numerical result $H_{\mathrm{num}}(X_{\mathrm{num}})$ at a given $X = X_{\mathrm{num}}$ proved after inspection to depend only on the variables D and $L_g \equiv 2s_g D/3s_c$, with $s_g = \lambda^{-1}(X)$ determined from eq 2.3, and *not* explicitly on K, P, or any of the other parameters. The relative deviation, as plotted in Figure 1, is fitted on the domain $0.02 \leq D \leq 0.2$, $L_g/D \geq 4$, and $L_g < 12$ to the form

$$R \simeq G_1/L_g + G_2/L_g^2 + G_3/L_g^3 + G_4 \ln L_g + G_5 + G_6 L_g \quad (3.1)$$

with

Figure 1. Relative deviation $R \equiv (H_{\mathrm{anal}} - H_{\mathrm{num}})/H_{\mathrm{num}}$, in percent, versus L_g.

Table 1. Coefficients of the Matrix in Eq 3.2

j	$k = 0$	$k = 1$	$k = 2$	$k = 3$	$k = 4$
1	−0.3643	−266.16	3029.4	−20659	53167
2	0.2092	−10.433	293.06	−1837.7	2308.1
3	−0.0195	1.2489	−23.680	138.08	−105.09
4	−2.1235	−330.89	8142.0	−64877	159756
5	−6.1076	1148.0	−22650	165126	−387535
6	1.0890	−0.0829	−302.47	3206.8	−8895.4

(The header row above spans γ_{jk}.)

$$G_j = \sum_{k=0}^{4} \gamma_{jk} D^k \quad (3.2)$$

The coefficients γ_{jk} are compiled in Table 1 (see also Figure 2). As the critical number of Kuhn segments at which excluded-volume effects start to influence the viscosity is still a matter of debate for wormlike chains,[22,23] a conservative upper bound of 12 is set on L_g. Multiplying the previously obtained analytical result (eq 2.17) by the correction factor $(1 + R)^{-1}$ yields a convenient approximation for the relative viscosity increment H accurate to within 1% (see Figure 3).
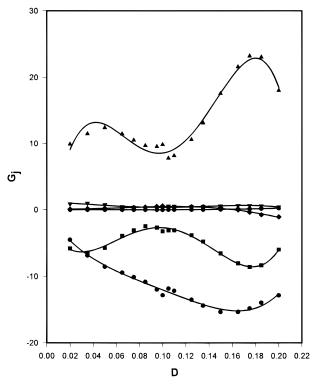
$$H_{\mathrm{theo}} = H_{\mathrm{anal}}(1 + R)^{-1} \quad (3.3)$$

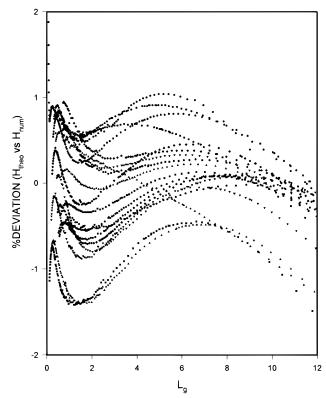This expression can be fitted to experimentally determined quantities.

Preliminary results for other values of n ($n = 3$ and $n = 6$) show a similar behavior. However, the analytical approximation is, on average, much more accurate at larger n and should therefore suffice as a fairly reliable theory when n is larger than unity.

4. Comparison with Experiment

Since micellar growth often occurs at fairly high concentrations, the practical use of the above theory is limited by the effects of higher-order terms in the

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Figure 2. Various G_j values versus reduced diameter D. For $D = 0.2$ they read from top to bottom: G_5, G_6, G_3, G_2, G_4, and G_1.

Figure 3. Percent deviation of H_{theo} with respect to H_{num} against L_g for $D = 0.02 - 0.2$ with step size 0.01.

concentration dependence of the viscosity. One way to tackle this problem is by accounting for the Huggins coefficient k_H. In a large number of experiments on various semiflexible polymers, k_H varies mainly between 0.40 and 0.50.[24−28] Choosing a value of $k_H = 0.45$ should therefore

Table 2. Comparison of the Fitted Theoretical Expression (Eq 3.3) with the Experimental Data Taken from Ref 12

n_s (M)	$\Delta X(\times 10^{-4})$	viscosity (cP)	H_{meas}	H_{exp}	H_{theo}
0.15	0	0.8109			
	1.622	0.8261	0.0187	0.0186	0.0179
	2.438	0.8384	0.0339	0.0334	0.0339
	3.253	0.8528	0.0517	0.0505	0.0520
	4.068	0.8694	0.0721	0.0699	0.0722
	5.699	0.9101	0.1223	0.1163	0.1185
	7.329	0.9638	0.1886	0.1748	0.1722
0.20	0	0.8164			
	0.8723	0.8350	0.0228	0.0226	0.0192
	1.6876	0.8610	0.0546	0.0533	0.0510
	2.5028	0.8966	0.0982	0.0942	0.0923
	3.3180	0.9401	0.1515	0.1424	0.1416
	4.1333	0.9909	0.2137	0.1964	0.1979
	5.7638	1.1204	0.3724	0.3249	0.3287
	7.3942	1.1265	0.5881	0.4831	0.4808
0.25	0	0.8262			
	0.8723	0.8670	0.0494	0.0483	0.0471
	1.6876	0.9230	0.1172	0.1116	0.1109
	2.5028	1.0060	0.2176	0.1997	0.2055
	4.1333	1.2701	0.5373	0.4473	0.4675
	5.7638	1.7631	1.1340	0.8266	0.8139
0.30	0	0.8357			
	0.9375	0.9102	0.0891	0.0858	0.0887
	1.7530	1.0446	0.2500	0.2268	0.2465
	2.5680	1.2909	0.5447	0.4525	0.4680
	3.3830	1.6907	1.0231	0.7619	0.7456

Table 3. End Cap Energies and Persistence Lengths from Our Theoretical Evaluation of the Data from Ref 12

n_s (M)	K	stand. dev	P (nm)	stand. dev
0.15	17.97	0.03	53	6
0.20	20.1	0.1	37	5
0.25	20.85	0.06	180	25
0.30	22.0	0.5	200	200

provide a reasonable way to eliminate first-order concentration effects:

$$H_{meas} = H_{exp}(1 + k_H H_{exp}) \qquad (4.1)$$

or

$$H_{exp} = \frac{-1 + (1 + 4k_H H_{meas})^{1/2}}{2k_H} \qquad (4.2)$$

Here, H_{meas} is the relative viscosity increment which is actually measured and we consider H_{exp}, corrected for concentration effects, as the relative viscosity increment which is to be compared to theory. This extends the concentration window considerably albeit in a semiempirical fashion.
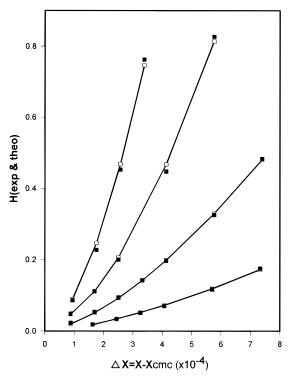
Accurate viscosity measurements on dodecylamine hydrochloride in water at $T = 303.15$ K and at various NaCl concentrations n_s were performed by Kushner et al. in 1957.[12] These authors found a Newtonian plateau.[29] A fit of H_{theo} (eq 3.3) to H_{exp}, obtained from eq 4.2, for $n = 1$, $\varnothing = 5$ nm, $s_c = 57$, and $C_0 = 5.5254$ mol·dL^{-1} gives the end cap energy K and the persistence length P at various ionic strengths (see Tables 2 and 3 and Figure 4). For comparison, results are included that do not strictly satisfy the restrictions of the theory. The standard

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Figure 4. Experimental relative viscosity increment (from ref 12) and the values obtained from the fits as explained in the text ($\blacksquare = H_{exp}$ and $\square = H_{theo}$). The lines are drawn to guide the eye.

deviations in Table 3 arise from the fit procedure. The data seem to conform well to the combined analytical and numerical theory summarized in eq 3.3. The quantities D and s_c have been constrained to reasonable values but should ideally be determined in an independent experiment to increase the accuracy of the other variables we wish to obtain.

One way to estimate either D or s_c when the other parameter is known is to view the micelles just above the cmc as monodisperse and spherical. The viscosity increment is then linear in ΔX

$$\text{for} \quad \Delta X \to 0 \quad H_{exp} \simeq \frac{5\pi D^3}{12 s_c} C_0 N_A \Delta X \qquad (4.3)$$

The fact that the slopes of the curves in Figure 4 are not equal as $\Delta X \to 0$ may be related to the salt dependence of the sphere-to-rod transition.

Note that in contrast to semiflexible polymers we have a strong dependence of the theoretical viscosity on the diameter of the micelle because of the relationship between it and the contour length, as expressed in eq 2.6.

We are now in a position to compare the ionic-strength dependence of the end cap energy with the theoretical predictions of Eriksson and Ljunggren[30] and independently Odijk[31] for highly charged micelles at intermediate ionic strengths ($0.02 \text{ M} \leq n_s \leq 0.3 \text{ M}$).
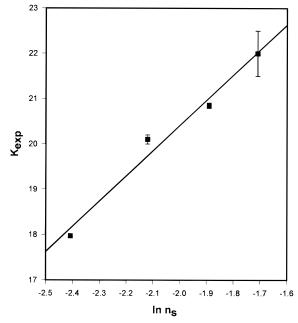
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(30) Eriksson, J. C.; Ljunggren, S. J. *Langmuir* **1990**, *6*, 895.
(31) Odijk, T. *Biophys. Chem.* **1991**, *41*, 23.

Figure 5.

$$K_{theo} = K_0 - \frac{2D}{Q}\ln\left(\frac{\pi Q \sigma}{\kappa}\right) \qquad (4.4)$$

Here K_0 is the bare end cap energy, $Q = 0.718$ nm is the Bjerrum length for water at $T = 303.15$ K, σ is the number of charges per unit area, and κ^2 equals $8\pi Q n_s$, relating the Debye screening length κ^{-1} to the monovalent salt concentration n_s. From eq 4.4, it follows that a plot of the end cap energy against the logarithm of the salt concentration should yield a straight line with a slope equal to DQ. As can be seen from Figure 5, the linearity holds for the cap energies in Table 3. The slope equals 5.56, which corresponds to a micellar diameter of approximately 4 nm, consistent with the value of 5.0 nm we chose a priori, since the former pertains to the electrostatic diameter and the latter to the hydrodynamic diameter.

5. Concluding Remarks

We have presented an analytical expression which, when combined with a numerically obtained correction factor, describes the zero-shear viscosity of a dilute solution of linear micelles. These calculations are unique in incorporating both the micellar polydispersity and semiflexibility.

An evaluation of the data by Kushner et al.,[12] neglecting any electrohydrodynamic effects, yields values of the end cap energy and the persistence length as functions of the ionic strength. The ionic-strength dependence of the end cap energy compares well with the theoretical work of Eriksson and Ljunggren[30] and Odijk.[31] In principle, eq 3.3 provides a straightforward way of extracting information concerning the growth parameters, stiffness, and dimensions of linear micelles from measurements of the viscosity as a function of amphiphile concentration. We stress again the restrictions of this work in terms of the average reduced length L_g and the reduced diameter D: $0.02 \leq D \leq 0.2$, $L_g/D \geq 4$, and $L_g < 12$.