

## QUANTITATIVE ANALYSIS OF ROD LIKE MICELLE SOLUTIONS VISCOSITY USING MICROSCOPIC PARAMETERS

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We modify the Hayter-Penfold formalism and gave a quantitative analysis to fit the viscosity of rod-like micelles solutions under shear using measured small-angle neutron scattering (SANS) intensity. The original formalism is applicable to a dilute solution, but we found that the theory can fit our measured results excellently if we use the effective viscosity of the solution in place of the solvent viscosity of the original formalism. The fittings yielded good values just the same as our experiment results.

### 1. Introduction

The structures and the phase transitions in self-assembling systems have attracted intensified interest over the course of the past decade. In certain surfactant-water systems micelles, which are initially spherical at low surfactant concentrations just above the critical micellar concentration, transform and undergo uniaxial growth as the concentration is increased to become cylindrical aggregates (worm-like) with a length that can be extremely long compared to their lateral dimensions.<sup>1</sup> In particular, surfactant molecules in aqueous solution display a rich variety of phenomena as they self-assemble to form micelles, of particular interest are the tubular-cylindrical micelles, their diameter is nearly constant but the length may vary, they break and reform continuously; hence they are sometimes called “living polymers”;<sup>2</sup> solutions of these micelles are thus stable when subjected to high mechanical shears and their equilibrium properties recover when shear is removed. In recent years several authors<sup>3</sup> found that for dilute solutions of these micelles under shear, viscosity would suddenly increase as the shear rate reaches a critical value. It is also found that such a transition depends sensitively on the sample conditions, such as the temperature, concentration, and salt concentration. Independent measurements, therefore, of the microstructure and the viscosity can not be easily correlated, and the nature of the transition was not fully understood. In addition, because of their

‘living’ nature, the structure and dynamics can change dramatically with concentration, or by the influence of a shear flow.<sup>4</sup>

Only recently, such studies have been performed on colloidal systems using microscopic techniques such as light<sup>7</sup> or neutron scattering.<sup>5,6,8</sup> The authors of Hayter and Penfold<sup>6</sup> have used viscous shear flow to align anisotropic micelles in normally isotropic phases and have studied the aligned micelles by small angle neutron scattering method. They presented results on dilute solutions of cylindrical micelles and develop a quantitative theoretical description of the scattering as a function of shear rate. Within their formalism, the orientational averaging is eliminated, which allows considerable simplification of the data interpretation, and the interactions between rods, such as collisions and other effects, are not taken into account either. We had studied the structure of cylindrical aqueous micellar solutions by small angle neutron scattering and light scattering both in equilibrium and under shear,<sup>5</sup> and found that for the 0.1%, which is just below the overlap concentration (the volume fraction of solutions) of the solutions, there is a threshold shear rate  $\gamma = 40s^{-1}$ , applied shear rate has little effect until the threshold shear rate is reached and then only after a time delay. We modified the viscosity as a function of shear while monitoring the microstructure with SANS, found that the system slightly below the overlap concentration goes through a phase transition at a certain critical shear rate at which point both the viscosity and the structure undergo a dramatic change. In order to explain the experimental results, we used the modified Hayter-Penfold expression, which differs from the original expression by a factor  $\alpha$ , the factor  $\alpha$  modifies the solvent viscosity  $\eta$  into an “effective viscosity”  $\alpha\eta$  to include the effects of interactions. And with the exponential length distribution, the model represents the data well at all shears. The fittings yielded good values just the same as our experiment results, and we can also describe the sub-macro characters indirectly from the experimental data using fitting method.

## 2. Calculation and conclusions

The scattering from solutions of anisotropic micelles is not generally calculable, even if the micelles are assumed to be monodisperse, but for dilute isotropic and non-interacting micelles solutions, the intensity  $S(Q)$  is<sup>9</sup>

$$S(Q) = \langle S(Q)_{l,\alpha} \rangle = A \int_0^{2\pi} d\phi \int_0^\pi \int_{l_0}^\infty p(\theta, \phi; P) F^2(Q, \beta) N(l) \sin \theta d\theta dl \quad (1)$$

The factor  $A$  is a product of an instrumental constant, the concentration of surfactants, the micellar aggregation number, and the square of the scattering length density contrast between the micelle and the solvent. For the length, the authors Lin et al. used the well known exponential form for living micelles given by

$$N(l) = \begin{cases} 0, & l < l_0 \\ N_0 \exp(-l/L), & l \geq l_0 \end{cases} \quad (2)$$

The form factor for a rod of radius  $a$  and half length  $l$ , and oriented in a direction which is an angle  $\beta$  from the vector  $Q$  is

$$F(Q, \beta) = \frac{\sin(Ql \cos \beta)}{Ql \cos \beta} \frac{J_1(Qa \sin \beta)}{Qa \sin \beta} \quad (3)$$

where  $J_1$  is the first Bessel function of the first kind. The brackets denote an average over both  $l$  and  $a$ . The  $\varphi$  is the angle between the wave vector  $Q$  and the horizontal axis of the area detector, and the relationship between  $\beta$  and the polar coordinates and  $\varphi$  is

$$\cos \beta_{\pm} = \sin \theta \cos \phi \cos \varphi \pm \cos \theta \sin \varphi \quad (4)$$

The two signs represent the beam traverses the sample twice in the shear cell, with the flow direction reversed in the two regions. And also we have

$$F^2(Q, \beta) = F^2(Q, \beta_+) + F^2(Q, \beta_-) \quad (5)$$

The term  $p(\beta)$  is the rod orientation probability, which in the equilibrium case, is independent of  $\beta$ , Hayter and Penfold<sup>6</sup> define the probability  $p(\beta) = p(\theta, \phi; P)$  in terms of the Péclet number,  $P = \gamma/D_\gamma$  as

$$p(\theta, \phi; P) = \frac{(1 - \cos 2\phi_0)(1 + \sin^2 \theta \cos 2\phi_0)^{3/2}}{4\pi[1 - \sin^2 \theta \cos 2\phi_0 \cos 2(\phi - \phi_0)]^2} \quad (6)$$

where the Péclet number  $P$  is the ratio of two competing rates between  $\gamma$ , which is the rate of the alignment rod in flow direction, and a randomizing rate assumed to be the rotational diffusion coefficient  $D_\gamma$ . In order to taken into account the interactions between rods, such as collisions and other effects, and provide a good representation of the experimental data, We defined the  $D_\gamma$  to be

$$D_r = \frac{ek_B T}{8\pi\alpha\eta l^3} \{\ln(2l/a) - 1.57 + 7[0.28 - 1/\ln(2l/a)]^2\} \quad (7)$$

which differs from the original Hayter Penfold expression by a factor  $\alpha$ . This factor modifies the solvent viscosity  $\eta$  to an “effective viscosity”  $\alpha\eta$  to include the effects of size and orientational distribution of the micelles under shear. The original formalism is applicable to a dilute solution and thus cannot account for a phase transition, but using the effective viscosity in place of the solvent viscosity in the original formalism can fit their results excellently.

In these formalism, there are five system parameters such as the experimental constant coefficient  $A$ , the introduced factor  $\alpha$  within the “effective viscosity”, and the geometric parameters of the micelles as the average half-length  $L$ , the low- $l$  cutoff  $l_0$ , and the radius  $a$ . All these parameters are important for the micelles solution system, and can not be measured directly during the experiments. So we then gave a quantitative analysis on them using a least squares method. The single scale factor  $A$  is determined by matching the experimental and theoretical intensities and is fixed for all other calculated curves. Fig. 1 compared the variation

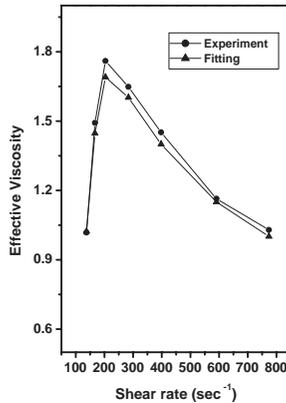


Fig. 1. Comparing micellar solutions viscosity between the measured and the fitted results, a phase transition occurs at a threshold shear rate around  $150\text{s}^{-1}$  where the viscosity increase dramatically.

of the effective viscosity between experimental and our fitting results, as a function of shear rate, just below the overlap concentration.

The fittings have yielded some good values, they agree well with the measured values, in that such a model can describe of such systems fairly well.

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### References

1. I. Wunderlich, H. Hoffmann and H. Rehage, *Reol. Acta* 26 (1987) 532
2. X.-I. Wu, C.Yeng, m.W.Kim, J.S.Huang, D.Ou-yang, *Phys. Rev. Lett.* 68(1992) 1426; I.A Kadoma, J.W.van Egmond, *Phys. Rev. Lett.* 76(1996) 4432
3. V. K. Jindal, J. Kalus, H. Pils, H. Hoffmann, P. Lindner, *Phys. J. Chem.* 94(1990) 3129; H. Rehage, I. Wunderlich, H. Hoffmann, *Prog. Colloid. Polym. Sci.* 72(1986) 51; M. Y. Lin, H. J. M. Hanley, S. K. Sinha, G. C. Straty, D. G. Peiffer, M. W. Kim, *Physica B* 213&214(1995) 613; C.-H. Liu, D. J. Pine, *Phys. Rev. Lett.* 77 (1996) 2121.
4. V. Schmitt, F. Lequeux, A. Pousse and D. Roux, *Langmuir* 10 (1994) 955; W. A. hamilton, P. D. Butler, S. M. Baker, G. S. Smith, J. B. Hayter, L. J. Magid and R. Pynn, *Phys. Rev. Lett.* 72 (1994) 2219
5. M. Y. Lin, H. J. M. Hanley, S. K. Sinha, G. C, Straty, etc. *Phys. Rev. E* 53(5) 1996, R4302
6. J. B. Hayter, J. penfold, *J. Phys. Chem.* 1984, 88, 4589-4593;
7. Clark, N. A.; Ackerson, B. J. *Phys. Rev. Lett.* 1980, 44, 1005; Hanley, H. J. M.; Rainwater, J. C.; Clark, N. A.; Ackerson, B. J. *J. Chem. Phys.* 1983, 79, 4448.
8. Oberthür, R. C. *Inst. Phys. Conf. Ser.* 1983, 64, 321; M. Y. Lin, H.J.M.Hanley, S. K. Sinha, G. C. Straty, D. G. Peiffer, M. W. Kim; *Physica B* 213& 214 (1995) 613-615.
9. See for example, G. Porod, in *Small Angle X-ray Scattering*, edited by O. Glatter and O. Kratky (Academic Press, New York, 1982)