J. Phys. Chem. A **2003,** *107,* 1133−1137

Effect of Pentanol and Salt on the Fusion−Scission Kinetics for CTAB Micelles

Bernard Michels and Gilles Waton*

Laboratoire de Dynamique des Fluides Complexes, UMR No. 7506, Université Louis Pasteur, CNRS, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

Received: February 5, 2002; In Final Form: November 27, 2002

The kinetic properties of aqueous solutions of CTAB with pentanol and KBr are studied with a T-jump device. The transition range from spherical to cylindrical micelles is determined with a microcalorimeter, and the semidilute range with an Oswald viscometer. The kinetic results show that, for elongated micelles, the value of the relaxation time decreases when the salt or pentanol concentration increases. This variation indicates that the decrease of the potential barrier is larger than the increase of the endcap energy. The observed variation of the potential barrier with salt concentration obeys a scale law, as expected by the DLVO theory. Its variation with pentanol obeys to a linear law. At the transition from spherical to cylindrical micelles the variation of the relaxation time is essentially controlled by the growth in the width of the length distribution.

It is well-known[1] that surfactant molecules self-assemble into micelles if the concentration is higher than the critical micelle concentration (cmc). The micelles can undergo uniaxial growth upon an increase of surfactant concentration[2] and upon addition of salt[3,4] or alcohol.[5,6]

It is also known that aggregates continuously exchange surfactant molecules with the bulk solution, and that the micelles break and merge. These kinetic processes have been widely investigated theoretically. The theoretical treatment of the exchange of surfactant molecules between micelles and solvent has been worked out by Aniansson et al.[7,8] Experimentally, these kinetics are generally studied by the ultrasonic relaxation absorption method.[9] Kahlweit has performed a theoretical study of the fusion−scission process[10,11] for spherical micelles, Cates[12] has theoretically studied wormlike micelles, and the relaxation time associated with the fusion-scission kinetics has been determined for some micellar shapes.[13]

Experimentally, these kinetics are investigated by the T-jump technique with light absorption detection in the case of the fusion−scission process of quasi-spherical micelles. Use of one absorbency probe is often necessary in this last technique. The fusion−scission kinetics can be studied without probes by the T-jump technique with light scattering detection, if the weight aggregation number of the micelles varies sufficiently with temperature. This last technique is the best suited for solutions of micelles from the dilute regime to the beginning of the semidilute regime, but it does not allow observation of the fusion−scission process of micelles when the micelles are strongly entangled.

The fusion−scission relaxation process has been studied in CTAB[14] solutions or in SDS[15] solutions at different temperatures and ionic strengths. These studies show that for elongated micelles the relaxation frequency increases as the square root of the average length of the micelles. For short micelles, the variation law of the relaxation time is unknown but it strongly depends on the size distribution of micelles. Zana et al.[16] studied the effect of alcohol molecules of different size on the relation process of surfactant solutions without salt.

The main purpose of the present paper is to study the change of the relaxation time associated with the fusion−scission process in CTAB micelle solutions when the addition of pentanol or KBr changes the size distribution.

Material and Methods

The micellar solutions were prepared, at high temperature, by dissolution of CTAB (cetyltrimethylammonium bromide) and pentanol in KBr brine. The measurements were performed at constant volume fraction of micelles (CTAB volume plus pentanol volume).

Differential Scanning Microcalorimetry (DSC). Measurements were made with a high sensitivity adiabatic differential scanning microcalorimeter[17] DASM-4 in the temperature range 30−100 °C with a heating rate of 1 °C/min. All samples showed an endothermic maximum of the heat capacity.

Viscosity. An Oswald-type device AVS 310 was used for the measurement of the flow time of the surfactant solutions though a calibrated capillary tube. The flow times were larger than 20 s and no kinetic correction was necessary when calculating the solution viscosity.

Relaxation Measurement. The temperature-jump (T-jump) device with Joule heating and monitoring of the relaxation via the change of intensity of scattered light has been described.[14] Measurements were performed at a 90° angle between incident and scattered light unless otherwise specified.

Experimental and Theoretical Background

DSC. In a previous paper,[18] we have shown that, in a CTAB solution, the presence of a maximum on the thermograms may be associated with the transition from rodlike to spherical micelles. Indeed, it is known that the aggregation number of CTAB micelles decreases when the temperature increases. Positive enthalpy energy is produced and new micelles are created by the breakdown of existing micelles. The energy output is low when the micelles are strongly elongated because the number of micelles is low and the increase of temperature creates few micelles. It is also low for spherical micelles that cannot divide. This energy output is a maximum when the

---

* To whom correspondence should be addressed. E-mail: Waton@ldfc.u-strasbg.fr.

10.1021/jp025600u CCC: $25.00

number of micelles is large and when the average size of the micelles is larger than spherical micelles. One can estimate that the average aggregation number of micelles at the peak temperature is about twice the aggregation number of spherical micelles. In the temperature range below the peak, the micelles are elongated; above the peak the micelles are nearly spherical.

Fusion−Scission Relaxation Process. For surfactant concentrations above the cmc, the relaxation time value of the fusion−scission process of micelles is linked to the size distribution of the micelles and to the kinetic parameters by[13]

$$\frac{1}{\tau} = \frac{m_w}{m_w - m} z k_f \tag{1}$$

where the average aggregation numbers m and m_w are respectively calculated in number and in weight, z is the number of micelles by volume unit, and k_f is the average probability of fusion.

For elongated micelles $m_w = 2m$ and the relaxation time is simply

$$\tau = \frac{1}{2zk_f} \tag{2}$$

zk_f is the probability that one micelle merges with one of z other micelles. At equilibrium, the number of micelles is constant, and this fusion probability must be equal to the probability that a micelle will break down. This equation is the same as Cates[12] equation:

$$\tau = \frac{1}{2zk_f} = \frac{1}{2k_b L} \tag{3}$$

where k_b is the scission probability by length unit and L is the average length of micelles.

For short micelles the product $m_w z$ is close to the number of surfactant molecules in the solution and the relaxation time depends on the variation of $m_w - m$, i.e., on the variation of the polydispersity.

Relation between Micelle Length and Relaxation Time. The average micelle length depends on the surfactant concentration C and on the energy of the endcap E:

$$L = \sqrt{C e^{E/kT}} \tag{4}$$

The fusion probability[19] depends on the collision frequency f_c and on the potential barrier E_p.

$$k_f = f_c e^{-E_p/kT} \tag{5}$$

The potential barrier is due to the interactions between micelles and to the successive conformational changes of micelles during the fusion or scission process. With eqs 4 and 5, eq 2 can be written

$$\tau = \frac{1}{\sqrt{C} f_c e^{-[(E/2)+E_p]/kT}} \tag{6}$$

Thus, at constant volume fraction of micelles, when E increases, the average micelle length increases and the relaxation time decreases.

Results and Discussion

Determination of Micelle Shape. Static measurements with the help of the DSC and viscosimeter were performed to state the domain where micelles have a spherical or an elongated shape. Of course, when pentanol is added[5,6] to a surfactant solution, the alcohol fits into the micelles. The shape of the micellar aggregates is changed and the size of micelles depends on the ratio R of the number of pentanol molecules to the number of surfactant molecules.

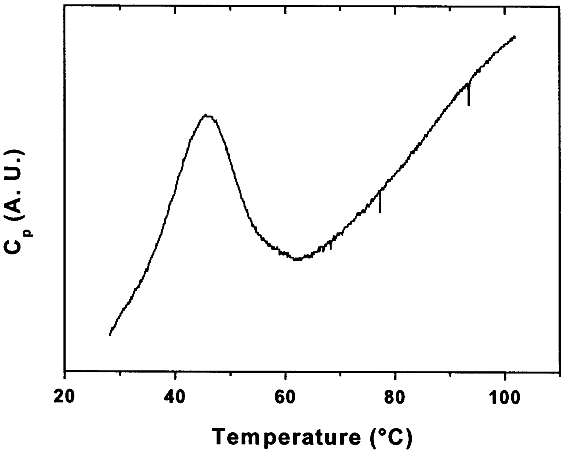

Figure 1. Temperature dependence of C_p for a micelle solution of CTAB−pentanol ($R = 1$) in 125 mM KBr.

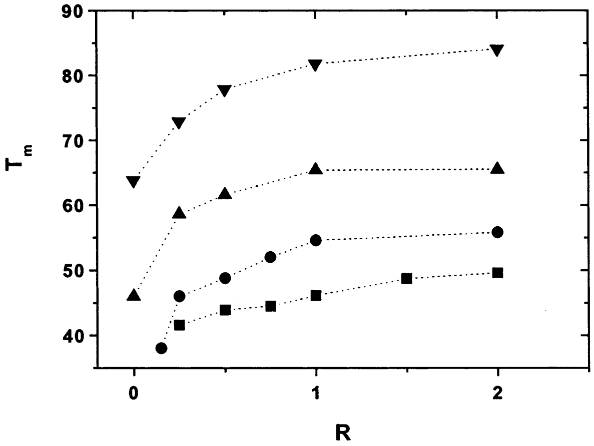

Figure 2. Temperature of peak thermogram T_m vs R at (■) 50, (●) 70, (▲) 100, and (▼) 200 mM KBr.

To determine the range where the transition from spherical micelles to cylindrical micelles occurs, thermograms of CTAB−pentanol solutions with a volume fraction of micelles equal to 3.6% were performed. Figure 1 shows the variation of specific heat with the temperature for a CTAB solution with pentanol in 50 mM KBr brine where the ratio R of the number of pentanol molecules to the number of CTAB molecules is 1. The specific heat value goes through a maximum at T_m. Two different contributions to the variation of the specific heat can be observed on this curve. One is associated with the decrease of micellar length when the temperature increases, which leads to a maximum of the specific heat. The other change of C_p value is due to the free surfactant molecules in the bulk. This last contribution may be attributed, in part, to the change of the cmc with temperature.

For all samples the shape of the C_p curves is very similar. Only the value of the temperature at which C_p attains a maximum is changed, and the curves can be superimposed by a temperature shift. Figure 2 shows the variation of the peak temperature T_m with the ratio R measured on pentanol CTAB solutions with a volume fraction of micelle equal to 3.6% and at four KBr concentrations (50−70−100−200 mM). The value of T_m increases with R and also with the KBr concentration.

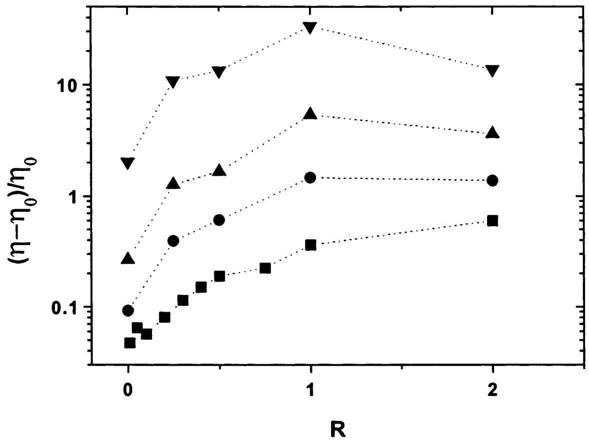

Figure 3. Relative viscosity vs *R* at (■) 50, (●) 70, (▲) 100, and (▼) 200 mM KBr.

At 100 and 200 mM KBr, microcalorimetric measurements show that the temperature transition from rodlike micelle to spherical micelles is always above 35 °C. At 50 and 70 mM KBr, without pentanol and even at small ratio *R*, the maximum is close to the Kraft temperature where the CTAB molecules crystallize and it cannot be measured.

The micelles are always very elongated in the semidilute regime, and to determine the solutions which are in this regime, the specific viscosity has been measured at 35 °C for different values of *R* and of KBr concentration; the resulting values are reported in Figure 3. The viscosity generally increases when the *R* or KBr concentration increases. However, for the largest values of *R* the viscosity decreases when *R* increases but the viscosity values are larger than at $R = 0$.

The change of the T_m values and of the viscosity with KBr concentration shows that the pentanol molecules fit into the micelle and produce an increase of the average length of micelles. The pentanol molecules slip between surfactant molecules at the surface of micelles. In the large range of *R* the decrease of the viscosity has been explained[16] by the incorporation of a part of pentanol molecules into the core of micelles. Indeed, the cosurfactant molecules solubilized in the core of micelles produce a swelling that increases the diameter of micelles and decreases the average length of micelles. As the measurements were carried out on solutions with a constant volume of CTAB + pentanol, this swelling reduces the entanglement of micelles and hence the viscosity decreases.

Kinetic Measurements. The T-jump experiments were performed on pentanol CTAB solutions with a volume fraction of micelles equal to 3.6% at 35 °C. The relaxation curve of the scattered light is always a monoexponential of decay time τ.

Figure 4 shows the variation of the relaxation times with *R* for 50−70−100 and 200 mM KBr concentrations. Two different behaviors of τ with *R* are observed depending on the KBr concentration. At 50 mM KBr, the relaxation time goes through a maximum versus *R* whereas it decreases over all the *R* range for 200 mM KBr. The variation of the relaxation time for 70 and 100 mM KBr concentration shows a halfway behavior.

Figure 5 illustrates the variation of the relaxation time with KBr concentration for two *R* values equal to 0 and 0.5. Two different behaviors are also observed.

Elongated Micelles. At 200 mM KBr for any *R* values and at $R = 0.5$ for any KBr concentration T_m is higher than 35 °C and the solutions are in the semidilute regime. Thus, the T-jump measurements at 35 °C were performed on solutions where micelles are always elongated and the relaxation time is given by eq 2.

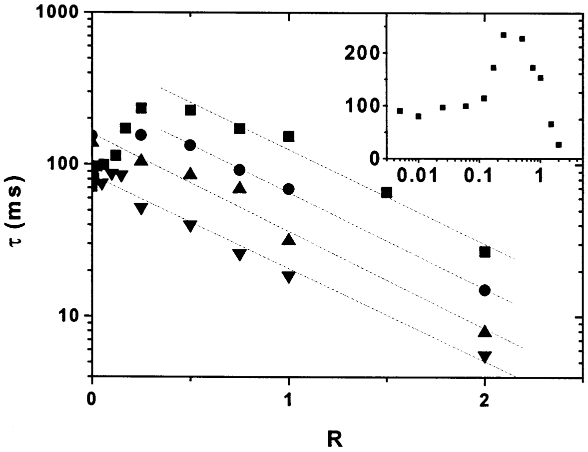

Figure 4. Relaxation time vs *R* at (■) 50, (●) 70, (▲) 100, and (▼) 200 mM. Inset: KBr = 50 mM KBr.

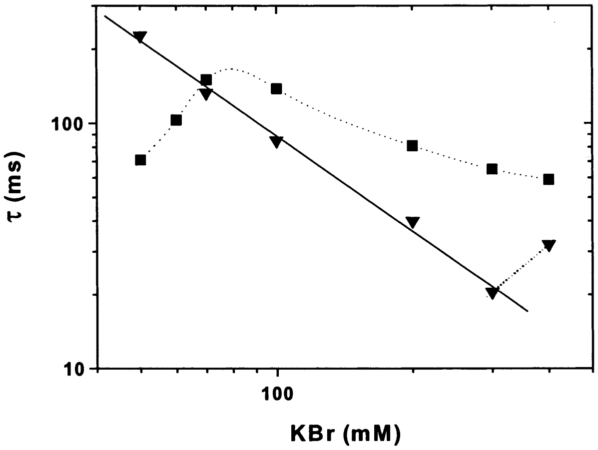

Figure 5. Relaxation time vs KBr concentration at $R = 0$ (■) and $R = 0.5$ (▼).

The measured variation of the relaxation time with *R* at 200mM KBr, observed in Figure 4 is given by

$$\ln(\tau) = 4.5 - 1.4R$$

At $R = 0.5$ the variation of the relaxation time with the KBr concentration reported in Figure 5 is

$$\ln(\tau) = 10 - 1.2\ \ln(C_{\mathrm{KBr}})$$

The relaxation time decreases and the average micelle length increases when *R* or C_{KBr} increases. This experimental observation shows that $E/2 + E_p$ decreases when E increases and that the decrease of E_p is larger than the increase of $E/2$.

The cationic CTAB micelles are charged and the electrostatic repulsion between the micelles decreases the fusion probability of micelles. According to the DLVO theory[20,21] the potential barrier, due to electrostatic repulsion, varies with the salt concentration as

$$\mathrm{e}^{-E_p/kT} = \left(\frac{C_s}{C_{s0}}\right)^s \qquad \text{for} \qquad C_s < C_{s0}$$

Where C_s is the salt concentration and C_{s0} is the critical salt concentration above which the potential barrier vanishes.

The exponent s and C_{s0} depend on the electrical surface potential of the endcap and on the valency of the ions of the electrolyte. C_{s0} depends also on the Hamaker[22] constant.

At $R = 0.5$ the variation of the relaxation time with KBr concentration obeys a scale law, as predicted by the DLVO theory. As the endcap energy E varies, a quantitative analysis of the exponent s and of C_{s0} cannot be conducted from the DLVO theory.

One can observe that at 400 mM KBr and $R = 0.5$ the relaxation time begins increasing. Around 300 mM KBr, the electrostatic repulsion begins to be low and the E_p variation with the KBr concentration is canceled by the variation of E.

Unfortunately, study of the variation of relaxation time for higher ionic strength, which depends only on the variation of E, cannot be performed because the variation of the diffused light with temperature is very low. Indeed, the micelles form a network and the light scattering intensity depends only weakly on the length of micelles. However, when the micelles are strongly entangled, the break time ($=1/k_b$), i.e., twice the relaxation time, can be obtained from rheological measurements. Candau et al.[23] performed rheological measures on CTAB solutions at high ionic strength, and they observed that the break time and the length of micelles increased with salt concentration.

For the measurement at variable R and constant KBr, $E_p + E/2$ decreases and the decrease of E_p is larger than the increase of E. The variation of E_p may be attributed to the change of the electrical surface potential induced by the addition of pentanol. This charge variation is difficult to assess because the distribution of pentanol molecules between the endcap and the cylindrical part of micelles is not known and because the ionization rate increases when the gap between the surfactant heads increases.

Another possibility to explain the variation of E_p is that one of the limiting steps is formation of a constriction on the cylindrical part. Pentanol is a short molecule and can undergo this step easier.

Spherical to Elongated Transition. At 50 mM KBr, in the low R range, the peak temperature T_m cannot be observed by microcalorimeter measurements because it is too close to the Kraft temperature, which is about 28 °C. For these R values, T_m is close to 35 °C and the shape of micelles is a short ellipsoid or a sphere. When R is above approximately 0.25, the peak on the thermogram can be observed at a temperature superior to 35 °C and the micelles are elongated. The addition of pentanol induced a change of the micelle shape: without alcohol the micelles are close to spherical shape and when the pentanol is add, the micelles become cylindrical.

The variation of the relaxation time with R when the micelle shape changes is very different from that observed with the elongated micelles. Instead of a monotonic decrease, the value of the relaxation time is nearly constant in the low R range, goes through a maximum for $R = 0.5$ and then decreases. For $R < 0.15$ the pentanol concentration is very low; the pentanol molecules are essentially in the bulk and the relaxation time does not change. At $R > 0.15$, pentanol molecules are incorporated in the CTAB micelles and induce the spherical micelle-elongated micelle transition.

For high R values, T_m is above 35 °C and the viscosity is high: the micelles are elongated.

In the transition range, the extremum of the relaxation time τ may be associated with the variation of the prefactor $(m_w - m_w)/m_w$ in the eq 1. Indeed, when the shape of the micelles is close to that of a sphere, the width of the length distribution is narrow and the prefactor value can be very low because m_w is close to m. When micelles are elongated, $(m_w - m_w)/m_w$ is equal to 1/2 and is independent of the average length of micelles. Thus the presence of a maximum on the relaxation time curve may be assigned to the increase of $(m_w - m_w)/m_w$ toward the asymptotic value 1/2.

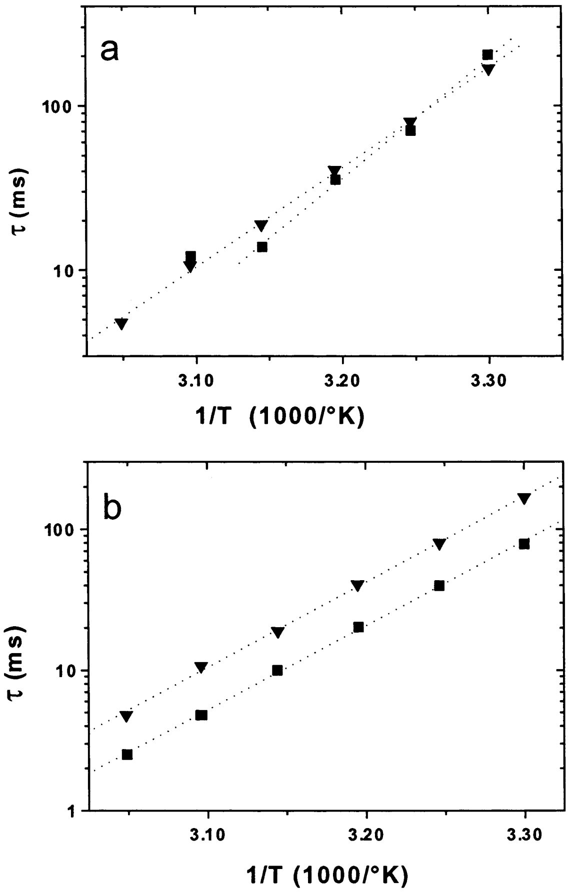

Figure 6. Relaxation time vs 1/T at (■) 50 and (▼) 200 mM KBr: (a) $R = 0$; (b) $R = 0.5$.

In the R range where the micelles are elongated, the variation of $E_p + E/2$ with R is linear and the slope -1.4 ± 0.05 is independent of the salt concentration.

When the transition from spherical to cylindrical micelles is induced by increasing salt concentration, the curve (inset Figure 4) of the relaxation time has a maximum as when the transition is induced by an R variation. As the relaxation time decreases in the semidilute regime, the variation of the prefactor $(m_w - m_w)/m_w$, during the spherical micelle to elongated micelle transition explains the presence of this maximum.

The variation of τ with the temperature is illustrated in Figure 6a for $R = 0$ and in Figure 7b for $R = 0.5$ at two KBr concentrations. The change of τ obeys an Arrhenius law for 200 mM KBr whereas at 50 mM KBr a departure from this law appears. At the low ionic strength, this deviation can be explained as follows: the measured relaxation time may depend not only on the change of the micelle length but also on the variation of $(m_w - m_w)/m_w$, which does not obey an Arrhenius law.

Viscosity and Relaxation Time Relations. In the static part of our study, we have noted that at large R the value of T_m is constant when the viscosity values decrease. These large values of T_m indicate that the micelles are elongated and exist as a living network. Also the viscosity[24,25] for these solutions depends not only on the size of micelles but also on the break probability of micelles. The break of a micelle allows reduction of the shear stress and leads to a lower value of the viscosity. Thus, at a constant value of micelle length, a decrease of τ, which corresponds to an increase of the break probability, leads to a

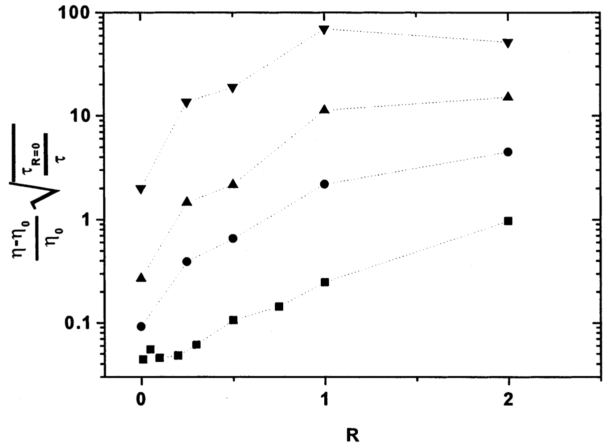

Figure 7. Relative viscosity divided by square root of the relaxation time normalized by its value at $R = 0$ vs R at (■) 50, (●) 70, (▲) 100, and (▼) 200 mM KBr.

decrease of the viscosity value. A model based on the tube model of polymer dynamics and including the effects of reversible scission kinetics has been derived by Cates.[26−28] This author has found that the zero shear viscosity is related to the plateau modulus, to the reptation time, and to the break time. He has shown that the viscosity value is proportional to the square root of the relaxation time of the fission−scission process. The viscosity measured with a capillary flow viscometer is not the zero shear viscosity but only an approximate value. However, the variation with the relaxation time of the measured viscosity must be similar. Finally, the values of the relative viscosity divided by $\sqrt{\tau}$ are reported on the Figure 7. The obtained values show that the micelle length changes only weakly with R for the large R values. These results agree with the T_m change reported in Figure 2.

Conclusion

This study of relaxation time shows that, for elongated micelles, the value of the relaxation time decreases when the salt or pentanol concentration increases. This variation indicates that the decrease of the potential barrier is larger than the increase of the endcap energy. The observed variation of the potential barrier with salt concentration obeys a scale law, as expected by the DLVO theory. Its variation with pentanol obeys to a linear law.

At the transition from spherical to cylindrical micelles the variation of the relaxation time is essentially controlled by the growth of the width of the length distribution.

References and Notes

(1) Israelachvili, J. N.; Mitchell, D, J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525.
(2) Rehage, H.; Hoffmann, H. J. *Phys. Chem*. **1988**, 92, 4712.
(3) Porte, G.; Appell, J.; Poggi, J. *J. Phys. Chem.* **1980**, *84*, 3105.
(4) Missel, P. J.; Mazer, N. A.; Benedek, G. B. *J. Phys. Chem.* **1980**, 84, 1044.
(5) Zana, R.; Yiv, S.; Strazielle, C.; Lianos, P. *J. Colloid Interface Sci.* **1981**, 80, 208.
(6) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* 1984, 101, 587.
(7) Aniansson, G. E. A.; Wall, S. *J. Phys. Chem.* **1974**, *78*, 1024
(8) Aniannson, G. E. A.; Wall, S. *J. Phys. Chem.* **1975**, *79*, 857.
(9) Frindi, M.; Michels, B.; Zana, R. *J. Phys. Chem.* **1992**, *96*, 6095.
(10) Kahlweit, M. *J. Colloid Interface Sci.* **1981**, *90*, 92.
(11) Kahlweit, M. *Pure Appl. Chem.* **1981**, *53*, 2069.
(12) Turner, M. S.; Cates, M. E. *J. Phys. France* **1990**, *51*, 307.
(13) Waton, G. *J. Phys. Chem.* **1997**, *101*, 9727.
(14) Faetibold, E.; Waton, G. *Langmuir* **1995**, *11*, 1972.
(15) Michels, B.; Waton, G. *J. Phys. Chem. B* **2000**,*104*, 228
(16) Lang, J.; Zana, R. *J. Phys. Chem.* **1986**, *90*, 5258
(17) Privalov, P. L.; Plotnikov, W.; Filiminov, V. J. *Chem. Thermodyn.* **1975**, *7*, 41.
(18) Faetibold, E.; Michels, B.; Waton, G. *J. Phys. Chem.* **1996**, *100*, 20063
(19) Fuchs, N. *Z. Phys.* **1934**, *89*, 736.
(20) Verwey, E. J.W; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: New York, 1948.
(21) Overbeek, J. Th. G. *Pure Appl. Chem.* **1980**, *52*, 1181.
(22) Hamaker, H. C. *Physica* **1937**, *4*, 1058
(23) Khatory, A.; Lequeux, F.; Kern, F.; Candau, S. J. *Langmuir* **1993**, *9*, 1456.
(24) Hoffmann, H.; Löbl, M.; Rehage, H. *Prog. Trends Rheol., 2nd Conf. Eur. Rheologists* **1986,** 246.
(25) Rehage, H.; Hoffmann, H. *Mol. Phys.* **1991**, 74, 933.
(26) Cates, M. E. *Macromolecules* **1987**, *20*, 2289.
(27) Cates, M. E. *Europhy. Lett.* **1987**, *4*, 497.
(28) Cates, M. E. *J. Phys. (Paris)* **1988**, *49*, 1593.