Microviscosity of Aqueous Surfactant Micelles: Effect of Various Parameters

R. Zana

Institut C. Sadron, CNRS−ULP, 6 rue Boussingault, 67000 Strasbourg, France

The microviscosity of aqueous micelles of 60 surfactants differing by the nature of the headgroup (cationic, anionic, nonionic, and zwitterionic), the carbon number of the surfactant alkyl chain, the nature of the counterion, and the chemical structure of the surfactant (conventional, bolaform, dimeric) has been investigated by fluorescence probing, using the viscosity-sensitive fluorescence emission of the probe 1,3-dipyrenylpropane (P3P). The microviscosity was taken as the product Q of the P3P excimer lifetime τ_E by the ratio I_M/I_E of the emission intensities of the P3P monomer and excimer forms, respectively. The energy of activation E^* of the microviscosity was obtained from the variation of Q with temperature in the range between 15 and 45 °C. The results for series of homologous surfactants showed that both Q and E^* increase with the alkyl chain length. The increment of E^* per additional methylene group in the alkyl chain was found to be independent of the nature of the surfactant series investigated and close to the increment of E^* for *n*-alkanes, for alkyl chains containing $8 \rightarrow 12$ carbon atoms, within the experimental error. This led to the conclusion that the large difference that exists between the values of Q for an *n*-alkane and the micelle of a surfactant having the same alkyl chain length is essentially due to the tethering of the surfactant alkyl chains to the micelle surface. Q varied in an irregular fashion with the size of the surfactant headgroup, but E^* was nearly independent of this parameter. In the case of the nonionic ethoxylated surfactant micelles, which possess a thick shell made of the polar heads, this result reveals that the probe is predominantly located in the micelle core, close to the micelle surface. The values of Q and E^* were found to be significantly lower for anionic surfactant micelles than for micelles of cationic, nonionic, and zwitterionic surfactants. The differences were attributed to a location of P3P somewhat closer to the surface of the micelle core of the latter surfactants, owing to the existence of attractive interactions between the probe and the surfactant polar heads. The results concerning the effects of the surfactant chain length, size of the polar head, and counterion nature showed the importance of the packing of the surfactant alkyl chains in determining the micelle microviscosity. Last, the microviscosity of micelles of cationic surfactants having the same chain length and headgroup was found to vary with the surfactant structure following the sequence: conventional surfactant < bolaform surfactant < dimeric surfactant.

Introduction

Surfactants self-associate in aqueous solution at concentrations above the critical micelle concentration (cmc) and give rise to micelles of various shapes. Close to the cmc the micelles are spherical or spheroidal. Upon increasing concentration they may retain this shape or become elongated or disklike depending on the nature of the surfactant. From micelles one can go to mixed micelles, micelles with solubilizates, and microemulsions upon introduction of additives, and to vesicles and lyotropic liquid crystals upon increasing the surfactant concentration.[1−3]

Micelles, microemulsions, and vesicles have been utilized as microreactors in which a wide range of chemical reactions have been performed after solubilizing the proper reactants in the assemblies.[4,5] Energy transfer and fluorescence quenching reactions have been much investigated as these reactions are important in topics as different as solar energy conversion[6] and proprties of aqueous micelles.[7−9] The rate of bimolecular reactions depends much on the polarity and viscosity of the medium in which the reaction takes place. It is usual to refer to the polarity and viscosity (or fluidity) within assemblies of amphiphiles as *micropolarity* and *microviscosity* (or *microfluidity*) since these assemblies are microscopic objects.[10−14] These properties can be conveniently investigated using the so-called fluorescence probing techniques which involve the introduction

in the medium under investigation of fluorescent probes having fluorescence properties, such as the intensity of emission, or the ratio of the intensities of two emission bands, or the wavelength at emission maximum, that are sensitive to some property of the environment.[7−9] J. K. Thomas pioneered the use of fluorescence probing for the study of micellar systems[15,16] as well as amphiphilic polymers[17] and surfaces.[18]

A number of fluorescence probes are characterized by fluorescence emission spectra that are sensitive to the viscosity of the probe environment. These probes can be applied to the study of the microviscosity of micellar systems. The microviscosity of micelles and vesicles can also be determined by means of other spectroscopic techniques such as EPR[19] and NMR.[20] Fluorescence probing remains the most often used method owing to its easiness.

Note that the concept of microviscosity has been criticized.[21−23] The main critic rests on the fact that most investigations of microviscosity involve probes that are solubilized in the organized assemblies and the use of a calibration plot representing the variation of a viscosity-sensitive property of the probe against the viscosity of a series of bulk solvent mixtures.[13,21,24−28] The microviscosity in a given system is then obtained from the measured value of the probe property in this system. The property of the probe depends on its location in the organized

TABLE 1: Values of the P3P Excimer Lifetime τ_E and of the Microviscosity Q at 15, 25, and 45 °C for the Surfactants Investigated and of the Activation Energy of the Microviscosity E^{*a}

		15 °C		25 °C		45 °C		
surfactant	C (wt %)	τ_E (ns)	Q (ns)	τ_E (ns)	Q (ns)	τ_E (ns)	Q (ns)	$E^{*\,m}$ (kJ/mol)
alkyltrimethylammonium bromide surfactants								
1. octytrimethylammonium bromide (OMe₃AB)[33]	15.64	82.7	434	74.4	230	60.8	83.7	41.6 ± 2
2. decyltrimethylammonium bromide (DeMe₃AB)[33]	4.80	81.2	513	75.0	277	60.4	93.0	43.3 ± 2
3. dodecyltrimethylammonium bromide (DMe₃AB)[33]	2.97	83.0	677	72.6	321	58.3	101	47.8 ± 2
4. tetradecyltrimethylammonium bromide (TMe₃AB)[33]	1.90	88.8	983	73.0	406	55.6	121	52.8 ± 3
5. hexadecyltrimethylammonium bromide (HMe₃AB)[33]	1.72	94.8	1218	76.6	519	57.0	136	56.0 ± 2
cationic bolaform surfactants								
6. hexadecanediyl-1,16-bis(trimethylammonium bromide) (H(Me₃AB)₂)[34]	7.41	105.5	1528	87.0	607	65.5	154	57.8 ± 3
7. eicosanediyl-1,20-bis(trimethylammonium bromide) (Eic(Me₃AB)₂)[35]	3.37	121.3	3323	93.7	902	69.2	204	58.6 ± 4
8. docosanediyl-1,22-bis(trimethylammonium bromide) (Doc(Me₃AB)₂)[36]	2.45	128.6	8180	100.4	1072	69.0	202	65.7 ± 5
quaternary ammonium bromide surfactants with two unequal chains								
9. dodecyldimethylethylammonium bromide (DMe₂EtAB)[33]	1.94	87.9	791	74.0	328	57.8	108	48.6 ± 3
10. dodecyldimethylpropylammonium bromide (DMe₂PrAB)[33]	2.21	88.5	751	74.7	344	59.7	112	48.6 ± 3
11. dodecyldimethylbutylammonium bromide (DMe₂BuAB)[33]	2.22	87.8	708	73.8	323	58.3	102	49.5 ± 2
12. dodecyldimethylpentylammonium bromide (DMe₂PeAB)[33]	2.45	84.4	651	71.5	307	58.5	112	43.6 ± 3
13. dodecyldimethylhexylammonium bromide (DMe₂HeAB)[33]	2.62	83.9	657	72.6	313	56.7	104	46.4 ± 2
14. dodecyldimethyl(6-hydroxyhexyl)ammonium bromide (DMe₂(HeOH)AB)[37]	3.32	94.9	1013	82.8	497	63.2	152	48.6 ± 2
15. dodecyldimethyloctylammonium bromide (DMe₂OAB)[33]	2.63	96.3	889	85.7	457	61.7	137	50.3 ± 2
quaternary ammonium bromide surfactants with increasing head group size								
16. tetradecyltriethylammonium bromide (TEt₃AB)[33]	1.42	96.5	1242	73.0	569	61.6	170	50.3 ± 2
17. tetradecyltripropylammonium bromide (TPr₃AB)[33]	1.46	98.7	1402	81.5	619	62.4	187	51.1 ± 2
18. tetradecyltributylammonium bromide (TBu₃AB)[33]	1.41	95.5	1274	79.7	589	60.6	172	50.5 ± 2
19. octadecyltripropylammonium bromide (OcPr₃AB)[b]	1.64	102.2	1957	83.9	858	63.9	241	53.2 ± 2
quaternary ammonium chloride surfactants								
20. dodecylammonium chloride (DAC)[38]	2.88	91.0	444	75.2	196	60.5	65.3	43.9 ± 5
21. dodecylmethylammonium chloride (DMeAC)[38]	3.07	92.4	515	77.8	240	59.8	107	32.5 ± 5
22. dodecyldimethylammonium chloride (DMe₂AC)[38]	2.94	92.7	542	77.6	265	61.4	92.1	45.8 ± 2
23. dodecyltrimethylammonium chloride (DMe₃AC)[38]	1.72	91.8	456	79.9	244	63.3	88.3	41.4 ± 1
24. hexadecyltrimethylammonium chloride (HMe₃AC)[39]	2.30	98.1	709	84.6	365			46.4 ± 4
25. hexadecylbenzyldimethylammonium chloride (HBeMe₂AC)[40]	2.47	104.8	918	86.1	449			50.7 ± 4
anionic surfactants								
26. potassium decanoate (KC₉CO₂)[41]	4.51	84.2	167	75.5	104	63.8	47.8	32.2 ± 1
27. rubidium decanoate (RbC₉CO₂)[41]	4.87	82.4	157	78.2	101	60.4	41.1	34.5 ± 1
28. sodium dodecanoate (NaC₁₁CO₂)[41]	2.94	89.5	141	77.5	82.1			38.2 ± 3
29. potassium dodecanoate (KC₁₁CO₂)[41]	2.52	84.4	179	77.9	116	61.8	48.2	33.9 ± 1
30. sodium octylbenzenesulfonate (NaO-Φ-SO₃)[c]	3.03	insoluble		81.7	173	66.5	75.8	34.2 ± 1
31. sodium dodecyl sulfate (NaDS)[d]	2.32	88.3	267	74.6	146	58.9	58.9	38.4 ± 1
32. hexylammonium dodecylsulfate (HeADS)[e]	0.505	81.5	236	66.6	108	54.8	44.4	35.3 ± 4
33. disodium tetradecylmalonate (Na₂TCH(CO₂)₂)[42]	1.35	96.3	301	82.6	165	66.1	60.8	42.8 ± 2
ethoxylated nonionic surfactants								
34. pentaethyleneglycol monooctylether (C₈E₅)[43]	9.70	92.0	392	77.3	210	57.0	81.7	42.4 ± 3
35. hexaethyleneglycol monooctylether (C₈E₆)[f]	10.29	96.2	437	81.4	228	63.9	90.9	40.0 ± 2
36. hexaethyleneglycol monodecylether (C₁₀E₆)[43]	4.60	98.3	537	79.5	259	58.9	99.5	42.4 ± 3
37. pentaethyleneglycol monododecylether (C₁₂E₅)[g]	4.19	99.5	612	80.5	289	two phases		53.2 ± 4
38. hexaethyleneglycol monododecylether (C₁₂E₆)[g]	5.87	101.4	642	81.8	317	57.6	99.8	47.0 ± 2
39. octaethyleneglycol monododecylether (C₁₂E₈)[g]	5.87	108.2	780	87.2	362	64.0	119	47.0 ± 2
40. nonaethyleneglycol monododecylether(C₁₂E₉)[g]	5.38	110.2	813	86.4	373	64.5	122	48.2 ± 3
41. Brij 35 (C₁₂E₂₃)[h]	9.75	121.7	1058	96.2	476	71.7	153	48.2 ± 2
42. octaethyleneglycol monohexadecylether (C₁₆E₈)[g]	5.26	122.1	1074	91.1	467	65.1	148	49.5 ± 3
43. Triton X100 (iO-Φ-EO₉.₅)[h]	4.87	163.6	3374	124.4	1413	83.0	315	61.2 ± 3
44. tyloxapol[h,i]	3.90	204.3	16300	180.9	7019	127.0	1400	62.2 ± 2
45. poly(ethyleneoxide) (PEO, $M_w = 600$)[j]	pure	solid	solid	132.7	2772	106.6	652	57.4 ± 4
sugar surfactants								
46. hecameg[44,45]	6.46	120.3	881	98.6	411			54.9 ± 4
47. octylglucoside (OG)[44,45]	5.01	113.1	714	93.9	334			55.3 ± 4
48. thiooctylglucoside (TOG)[45]	3.22	121.3	832	98.7	402			51.8 ± 4
49. octanoylmethylglucamid (OMeGlu)[45]	4.62	119.8	777	99.7	419			45.3 ± 4
50. dodecylmaltoside (DM)[44]	2.50	164.2	3816	128.1	1458			70.7 ± 6
zwitterionic surfactants								
51. octyldimethylammoniopropanesulfonate (OMe₂APrSO₃)[46]	13.63	105.6	708	90.5	352	69.7	119	45.2 ± 2
52. decyldimethylammoniopropanesulfonate (DeMe₂APrSO₃)[46]	3.63	106.4	815	90.1	410	68.3	128	47.0 ± 1
53. dodecyldimethylammoniopropanesulfonate (DMe₂APrSO₃)[47]	2.12	115.2	1244	94.4	581	68.8	172	50.7 ± 2
54. α-dodecyldimethylammonio-ω-methanecarboxylate (DMe₂AMeCO₂)[47]	2.05	104.7	916	89.4	442	62.8	126	50.7 ± 2
55. α-dodecyldimethylammonio-ω-propanecarboxylate (DMe₂APrCO₂)[47]	1.98	106.5	831	91.3	415	66.1	132	46.6 ± 2
56. α-dodecyldimethylammonio-ω-pentanecarboxylate (DMe₂APeCO₂)[47]	2.17	112.0	961	94.2	470	68.5	149	47.8 ± 2
57. α-dodecyldimethylammonio-ω-decanecarboxylate (DMe₂ADeCO₂)[47]	2.36	118.5	985	96.9	476	71.8	149	47.8 ± 2
58. decyldimethylamineoxide (DeMe₂AO)[k]	4.81	97.5	481	82.0	244	64.7	89.9	42.2 ± 2

Aqueous Surfactant Micelles

J. Phys. Chem. B, Vol. 103, No. 43, 1999 **9119**

TABLE 1 (Continued)

		15 °C		25 °C		45 °C		
surfactant	C (wt %)	τ_E (ns)	Q (ns)	τ_E (ns)	Q (ns)	τ_E (ns)	Q (ns)	$E^{*\,m}$ (kJ/mol)
				cationic dimeric surfactants				
59. 8-6-8, 2Br⁻ [l,29]	4.07	92.0	736	80.5	366	64.0	123	45.3 ± 2
60. 12-6-12, 2Br⁻ [l,29]	2.12	95.7	1675	83.2	778	64.4	235	49.9 ± 2
61. 16-6-16, 2Br⁻ [l,29]	2.12	101.8	2830	87.7	1228	64.4	301	56.6 ± 2
				n-alkanes				
62. *n*-octane	pure	11.7	28.1	10.7	20.5	9.3	12.3	20.4 ± 1
63. *n*-dodecane	pure	21.9	52.1	19.0	35	15.3	18.7	26.2 ± 1

[a] Abbreviations used. Me, Et, Pr, Bu, O, iO, De, D, T, H, Eic, Doc = methyl, ethyl, propyl, butyl, octyl, iso-octyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, docosyl. Be: benzyl. Φ: phenylene. B: bromide. C: chloride. A: ammonium or ammonio. E: ethoxy. [b] Prepared by reacting octadecylbromide with tripropylamine.[33] [c] Gift from Dr. N. Kamenka, University of Montpellier, France. [d] From Touzart-Matignon (France), recrystallized from ethanol. [e] Prepared by stoichiometric neutralization of dodecylsulfuric acid by *n*-hexylamine (Fluka). The dodecylsulfuric acid was obtained by passing an aqueous solution of SDS through a strong cation exchange resin Merck in the acid form. [f] Gift from Dr. E. Platone (EniRicerche, Milan, Italy). [g] Purchased from Nikko (Tokyo). [h] Purchased from Sigma. [i] No maximum was observed for the excimer emission at 15 °C. The excimer intensity was measured at 485 nm. [j] From Hoechst (Germany). [k] Gift from Pr. J. Desnoyers (University of Sherbrooke, Canada). [l] Dimeric surfactants of the alkanediyl-α,ω-bis(alkyldimethylammonium bromide), referred to as *m-s-m*, 2Br⁻. [m] The uncertainty on E^* depends on the quality of the linearity of the ln Q vs $1/T$ plot. The errors are larger for those systems where E^* was determined in a more restricted range of temperature.

assembly which is *microheterogeneous* in nature. Different probes are preferentially located at different sites in the assembly and are therefore expected to report different values of the microviscosity, as was indeed observed.[21] Nevertheless, microviscosity studies remain meaningful for investigations involving series of homologous surfactants such as surfactants having the same chemical structure and headgroup but of varying alkyl chain length or surfactants having the same headgroup and chain length but of differing chemical structure. Then, as was shown in previous studies,[22,29] different methods of measuring microviscosities can be made to yield similar results. Microviscosity data thus obtained have been useful for explaining the very low values found for the quenching rate constants within micelles of quaternary ammonium surfactant oligomers and within hydrophobic microdomains present in aqueous solutions of polysoaps.[29] Another critique of the concept of microviscosity concerns the fact that the probe senses the microviscosity of a medium that is perturbed by its mere presence. Again it can be argued that this critique is minimized when investigating series of homologous surfactants. Nevertheless, the results for different surfactant series can be compared only with much caution.

The aim of the present work was to determine how the micelle microviscosity varies with the alkyl chain length of the surfactant, the nature of its headgroup and counterion, the surfactant chemical structure, and the temperature. The study reported below has involved a total of sixty surfactants, anionic, cationic, nonionic, and zwitterionic, and is probably the most comprehensive to date. The results were obtained using the well-known, viscosity-sensitive fluorescent probe 1,3-di(1-pyrenylpropane) (P3P).[13,14,26,29–32] The results show that the microviscosity varies little with the surfactant concentration when no gross change of micelle size occurs, increases with the surfactant alkyl chain length for all surfactant series irrespective of the nature of the headgroup, decreases upon increasing temperature, depends in a complicated manner on the size of the headgroup and nature of the counterion for the different surfactant series, and depends on the surfactant chemical structure. This study complements a previous one on quaternary ammonium surfactant oligomers.[29]

Experimental Section

Materials. The surfactants investigated are listed in Table 1. Their origin is specified by references to previous studies[29,33–47] and in the footnotes of the table. As can be seen a large part of

the present work concerned cationic surfactants because they have been synthesized with a great variety of structures, well purified, and much investigated in our laboratory in the past 20 years.[29,33–40] *n*-Octane and *n*-dodecane were from Aldrich. The sample of liquid poly(ethylene oxide) (PEO, molecular weight 600) was from Hoechst. The compounds investigated are referred to below using the number they are given in Table 1. The fluorescent probe P3P was obtained from Molecular Probes (Eugene, Oregon) and used as received.

The surfactant content of the solutions was generally between 1 and 3 wt %. However values as high as 10–15 wt % were used for solutions of surfactants with high molecular weight and/or high cmc values, such as short chains ionic and nonionic surfactants.

The solutions for fluorescence probing studies were prepared by injecting the appropriate amount of a P3P stock solution in tetrahydrofuran in the investigated aqueous surfactant solution which was then stirred at 30 °C at least for 12 h.[29] The injected volume amounted to less than 0.5% of the volume of solution. We checked that this small amount of tetrahydrofuran had no effect on the measured properties. This procedure gave more reproducible results than the usual one (introduction of an appropriate volume of probe solution in an organic solvent into an empty flask, evaporation of the solvent, introduction of the surfactant solution, and probe solubilization by stirring). Indeed, the solubilization of very hydrophobic probes from the solid state may require days or weeks and incomplete solubilization can cause severe errors in the measured quantities.[48,49]

Method. The emission spectrum of P3P shows four peaks located between 370 and 395 nm and corresponding to the vibronic emission of the probe monomer and a large band centered around 485–490 nm which corresponds to the probe excimer emission. For P3P, the quantity $Q = \tau_E I_M / I_E$ (τ_E = excimer fluorescence lifetime; I_M and I_E = intensities of the emission of the monomer and excimer forms of P3P) is theoretically proportional to the microviscosity.[26,31] In this paper Q is referred to as microviscosity. The P3P concentration in the investigated solutions was of $1-2$ μM. The overall experimental error on Q is estimated to be of ± 5%.

The fluorescence intensities were measured using a Hitachi F-1040 spectrofluorometer. P3P was excited at 346 nm and the emission monitored between 350 and 550 nm. The intensites I_M and I_E were obtained from the emission spectrum at the wavelengths corresponding to the first vibronic peak of the

TABLE 2: Comparison of the Values of the P3P Excimer Lifetime τ_E of the Intensity Ratio I_M/I_E and of the Microviscosity $Q = \tau_E I_M/I_E$, in Air-Saturated and Argon-Saturated Solutions for Selected Surfactants at 25 °C

surfactant	air-saturated			argon-saturated		
	τ_E (ns)	I_M/I_E	Q (ns)	τ_E (ns)	I_M/I_E	Q (ns)
BHDC	87.1	5.21	453	115.5	4.19	483
DM	128.1	11.38	1457	151.6	10.1	1535
hecameg	98.6	4.17	411	119.2	3.61	429
TOG	98.7	4.07	402	121.6	3.49	425
OMeGlu	99.7	4.20	419	120.2	3.61	434
tyloxapol	181	35	6330	195.4	33.9	6620

monomer form, located near 378 nm, and to the excimer form at around 490 nm. The excimer fluorescence lifetime τ_E was measured at an excitation wavelength of 335 nm and at an emission monitored at above 460 nm, using the Kodak gelatin filter 4, by means of a single-photon-counting apparatus.[38−40] As in other studies,[14,31] the plots of the fluorescence intensity versus time showed first an increase of intensity at short times arising from the excimer growth upon excitation and a decrease of intensity corresponding to the decay of the excimer fluorescence. The excimer lifetime was obtained from the decaying part of the plots. For most systems the decays were single exponential. However, in some instances, particularly at high temperature, the decays showed the occurrence of a longer component of small amplitude. The values of τ_E listed in Table 1 all refer to the first decay component.

The lifetime and intensity measurements were generally performed at 15, 25, and 45 °C on air-saturated systems. We have compared for selected systems the values of the microviscosity Q for air-saturated and argon-saturated solutions. Indeed, the quenching of the P3P fluorescence by molecular oxygen, which affects the lifetime and intensity values, does not take place in the argon-saturated systems. The results are listed in Table 2. It is seen that the larger τ_E values in argon-saturated systems are largely compensated by the larger values of I_M/I_E in air-saturated systems. Nevertheless, a small, 4−6%, but systematic difference is seen between the two sets of Q values, the air-saturated solutions showing smaller values than the argon-saturated solutions. Such a difference was in most instances smaller than the variations that were observed when changing the surfactant characteristics (see below) and, therefore, the experiments used air-saturated solutions.

Results and Discussion

We have checked for several surfactant solutions that, as expected, the microviscosity Q is independent of the P3P concentration in the range between 0.18 and 1.8 μM. This is illustrated in Figure 1 for DMe$_3$AB (surfactant **3**). Most measurements were performed at a P3P concentration close to 1.8 μM where the fluorescence intensities are large and easy to measure accurately.

The values of the P3P excimer lifetime and of the micelle microviscosity are listed in Table 1 for all the compounds investigated. The results for the anionic surfactants are less extensive than for the other surfactants because P3P was not soluble in solutions of anionic surfactants with $m = 7$ and because the Krafft temperature of anionic surfactants with $m = 13$ is above room temperature. For the sake of comparison we have also determined the values of Q in liquid PEO, n-octane, and n-dodecane (compounds **45**, **62**, and **63** in Table 1).

Effect of the Surfactant Concentration. Figures 2 and 3 show that the microviscosity of ionic and of ethoxylated nonionic surfactant micelles is independent of the surfactant
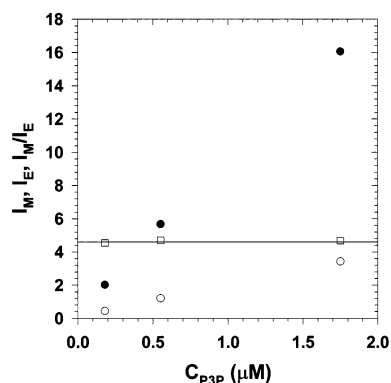
Figure 1. Variations of I_M (●) and I_E (○) (both in arbitrary units) and of the ratio I_M/I_E (□) with the P3P concentration for a 3 wt % solution of DTAB, at 25 °C.
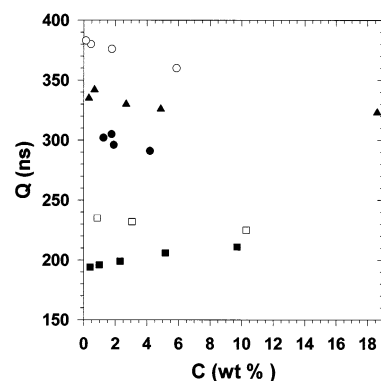
Figure 2. Effect of the surfactant concentration on micellar microviscosity measured for solutions of C$_8$E$_5$ (**34**, ■), C$_8$E$_6$ (**35**, □), C$_{12}$E$_5$ (**37**, ●), and C$_{12}$E$_8$ (**39**, ○) at 25 °C, and TX100 (**43**, ▲), at 45 °C.
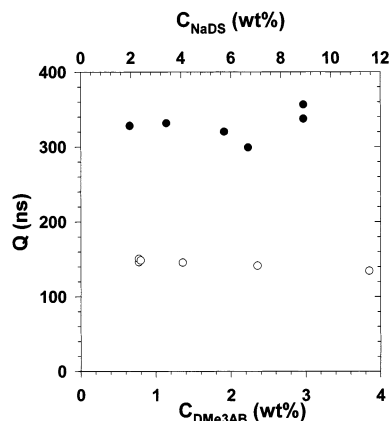
Figure 3. Effect of the surfactant concentration on the micellar microviscosity for solutions of DMe$_3$AB (**3**, ●) and NaDS (**31**, ○), at 25 °C.

concentration, within the experimental error. Such a behavior is to be expected if the probe is fully micelle-solubilized and if the micelles do not undergo too large changes of size and shape upon increasing surfactant concentration in the range investigated. This is indeed the case for the surfactants in Figures 2 and 3. Similar results have been reported for other surfactants by Miyagishi et al.[26,27,50−54] who used auramine as viscosity-sensitive fluorescent probe. However, it has been shown[26,29,51−54] that the microviscosity increases when the micelles grow in size and become elongated and entangled upon increasing surfactant concentration. At very high concentration when the transformation is achieved, the microviscosity levels out.

Effect of Temperature. The data listed in Table 1 show that the microviscosity Q always decreases upon increasing tem-

Aqueous Surfactant Micelles

*J. Phys. Chem. B, Vol. 103, No. 43, 1999* **9121**
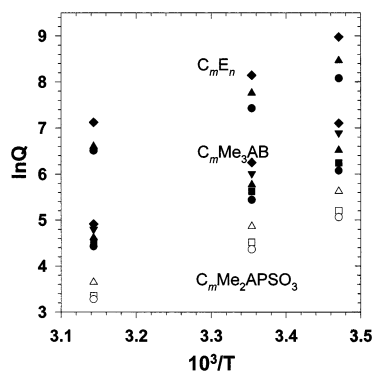
Figure 4. Effect of temperature on the microviscosity of micellar solutions of surfactants of differing alkyl chain length: cationic surfactants C_mMe_3AB with $m = 8$ (●), 10 (■), 12 (▲), 14 (▼), and 16 (◆); nonionic surfactants C_mE_n: C_8E_6 (●), $C_{12}E_6$ (▲), and $C_{16}E_8$ (◆), and zwitterionic surfactants $C_mMe_2APSO_3$ with $m = 8$ (○), 10 (□), and 12 (△). The ln Q values for the nonionic and zwitterionic surfactants have been shifted by 2.0 and −1.5 units respectively, for the sake of clarity.
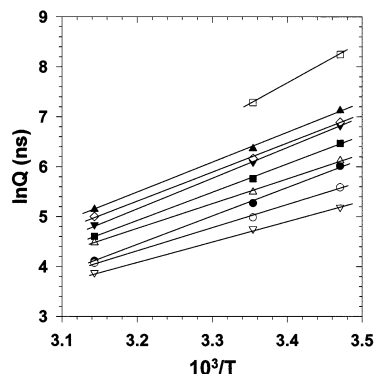

Figure 5. Effect of temperature on the microviscosity of various surfactants having a dodecyl alkyl chain: Dodecylmaltoside (**50**, □), DMe_2APrSO_3 (**53**, ▲), DMe_2ADeCO_2 (**57**, ◇), DMe_2AMeCO_2 (**54**, ▼), $C_{12}E_6$ (**38**, ■), DMe_3AC (**23**, △), DMe_3AB (**3**, ●), NaDS (**31**, ○), and $KC_{11}CO_2$ (**29**, ▽).
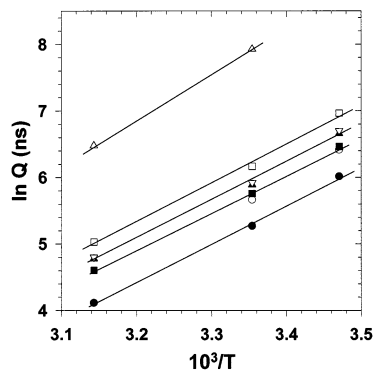
Figure 6. Effect of temperature on the microviscosity of various $C_{12}E_n$ surfactants: $C_{12}E_5$ (**37**, ○); $C_{12}E_6$ (**38**, ■), $C_{12}E_8$ (**39**, ▲), $C_{12}E_9$ (**40**, ▽), and $C_{12}E_{23}$ (**41**, □). For the sake of comparison the results for DMe_3-AB (**3**, ●) and PEO (**45**, △) are also given.

perature (T), similarly to the viscosity of usual fluids. The plots of ln Q vs $1/T$ are linear in the range investigated (see Figures 4−6), except for the surfactants **7**, **8**, **20**, **21**, and **32**. For these surfactants experimental errors, or the approach of the Krafft temperature (see below) are probably responsible for the nonlinearity of the plots. For the other surfactants, the linearity of the plots permitted us to write
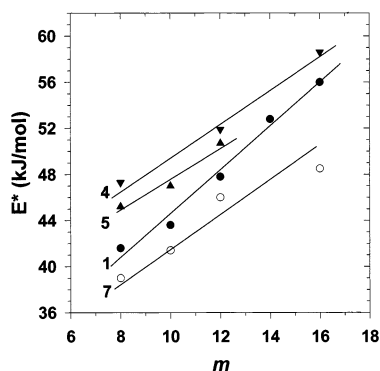
$$Q = Q_0\exp(-E^*/kT) \qquad (1)$$
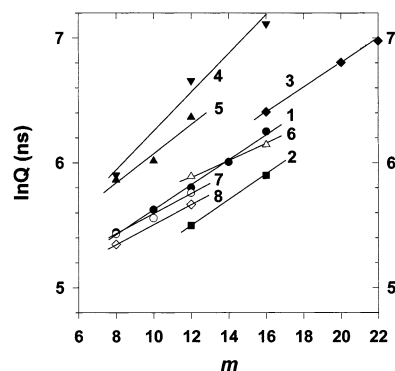
Figure 7. Effect of the surfactant chain length on the micelle microviscosity for (1) C_mMe_3AB surfactants **1−5** (●), (2) C_mMe_3AC surfactants **23** and **24** (■), (3) bolaform surfactants **6−8** (◆): (4) dimeric surfactants m-6-m, $2Br^-$ **59−61** (▼), (5) $C_mMe_2APrSO_3$ zwitterionic surfactants **51−53** (▲), (6) C_mE_8 (△), (7) C_mE_6 (○), and (8) C_mE_5 (◇) at 25 °C. The solid lines are guides to the eyes.

where E^* has the meaning of an activation energy for the microviscosity. The ln Q vs $1/T$ plots yielded the E^* values listed in Table 1. In those instances where the plot was not linear over the range 15−45 °C, E^* was calculated from the results in the range 25−45 °C. The values of E^* are discussed together with the values of Q.

Effect of the Surfactant Chain Length. Figure 4 shows that at a given temperature Q increases with the carbon number m of the surfactant alkyl chain, irrespective of the surfactant nature: cationic (conventional, bolaform, and dimeric), nonionic, and zwitterionic. Table 1 shows similar increases of Q with m for other cationic surfactant series (surfactants **17** and **19**; surfactants **23** and **24**), and the anionic surfactants **26** and **29**. A similar result was obtained for the cationic surfactants C_m-Me_3AB in an EPR spectroscopy study using micelle-solubilized nitroxide probes.[24]

The value of Q also increases in going from n-octane to n-dodecane (compounds **62** and **63**). However, the values of Q for these two alkanes are more than 1 order of magnitude smaller than for micelles of surfactants having the same carbon number, except for the anionic surfactants where the difference is smaller (factor 5). Thus, at 25 °C the values of Q for surfactants with $m = 8$ would be around 100 ns for anionic surfactants and range between 200 and 400 ns for the other surfactants, as compared 20.5 ns for n-octane. This result confirms that the microviscosity of micelles is much larger than the viscosity of the bulk alkane with the same carbon number as the surfactant.[13,21,26,27,29,31] Note that the ratio of the Q values for the two alkanes is smaller than the ratio of their bulk viscosities (1.63 vs 2.56[55] at 25 °C). Also the value of E^* for Q is much larger than the activation energy for the viscosity of bulk n-octane (8.7 kJ/mol).[55] These two results indicate that the viscosity sensed by P3P in bulk solvents is not exactly that determined by conventional techniques.

The results represented in Figure 7 show that the increase of Q with m for several surfactant series is nearly linear in the semilogarithmic representation used. The various plots have about the same slope, to within 20%, despite the strongly differing nature of the surfactant series considered: conventional cationics (C_mMe_3AB, C_mMe_3AC) and zwitterionics (C_mMe_2APr-SO_3), bolaforms ($C_m(Me_3AB)_2$), surfactant dimers, and nonionics (C_mE_n). The slopes of the plots for the three nonionic series are slightly smaller than for the other surfactant series. The few results available for the anionic surfactants show that the variation of Q with m is much smaller than for the other

Figure 8. Effect of the surfactant chain length on the activation energy of the micelle microviscosity for (1) C_mMe_3AB (●); (4) dimeric surfactants m-6-m, $2Br^-$ (▼, shifted by $+2$ kJ/mol); (5) zwitterionic surfactants $C_mMe_2APrSO_3$ (▲); and (7) C_mE_6 (○, shifted by -1 kJ/mol). The solid lines are guides to the eyes.

Figure 9. Effect of the size of the surfactant headgroup on the micelle microviscosity for the series of cationic $C_{14}(C_nH_{2n+1})_3AB$ (●) and $C_{12}H_{3-n}(CH_3)_nAC$ (▲), nonionic $C_{12}E_n$ (■) and zwitterionic $C_{12}Me_2$-$NC_nH_{2n}CO_2$ (△) surfactants at 25 °C.

surfactants (see Table 1). Figure 4 shows that the effect of m on the microviscosity tends to decrease as the temperature is increased.

The E^* values listed in Table 1 show that the activation energy E^* also increases with the surfactant chain length for all the surfactant series investigated, irrespective of the surfactant nature and chemical structure. Figure 8 shows that this increase is nearly linear for several surfactant series. One can thus write:

$$E^* \approx a + bm \qquad (2)$$

Besides, the plots in Figure 8 have nearly the same slope to within 20%. Thus nearly parallel plots are expected for the variation of ln Q with m, and are indeed seen in Figure 7. The average value of the slopes of the plots in Figure 8 is equal to 1.85 ± 0.3 kJ/mol CH_2. A somewhat smaller value of 1.6 ± 0.3 kJ/mol CH_2 is obtained when considering only the data between $m = 8$ and 12. This last value of the increment of E^* is rather close to that obtained from the values of E^* for n-octane and n-dodecane: 1.45 kJ/mol CH_2, even though the values of Q and E^* for the n-alkanes are much smaller than for the surfactant micelles.

A tentative explanation for the increase of Q with m is as follows. The formation of a P3P intramolecular excimer involves a motion of the two pyrenyl moieties of P3P which is similar to that of the wings of a butterfly. This motion requires a displacement of surfactant alkyl chains in the immediate surrounding of the probe. It is clear that the pyrenyl moiety motion becomes increasingly difficult as the carbon number m of the alkyl chains increases because they are then more and more entangled and tightly packed and also because their molecular weight increases. Similar explanations were proposed for the increase of microviscosity of micelles of conventional surfactants undergoing a sphere-to-cylinder transformation upon increasing surfactant concentration,[27,29,51−54] and of surfactant oligomers upon increasing degree of oligomerization.[29] These various factors are present in both surfactant micelles and bulk n-alkanes. However in the former the surfactant alkyl chains are tethered to the micelle surface through the headgroups. One is thus led to assign to this tethering to the micelle surface most of the difference in the values of Q and E^* characterizing surfactant micelles and n-alkanes.

Effect of the Size of the Surfactant Headgroup. This effect can be seen in three series of surfactants: the cationics C_{14}-$(C_nH_{2n+1})_3AB$ (surfactants **4** and **16−18**) and $C_{12}H_{3-n}(CH_3)_nAC$ (surfactants **20−23**), the nonionics $C_{12}E_n$ (surfactants **37−41**), and the zwitterionics $C_{12}Me_2NC_nH_{2n}CO_2$ (surfactants **54−57**).
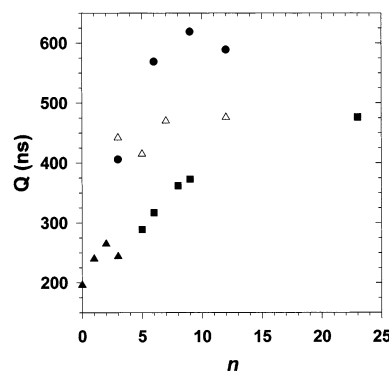
The results at 25 °C are represented in Figure 9 as function of the parameter n which characterizes the size of the headgroup (number of methyl plus methylene groups for the cationic and zwitterionic surfactants, number of ethoxy groups for the nonionic surfactants, in the headgroup). The variations of Q with n are much dependent on the nature of the surfactant with the presence of a maximum for the cationics, of a minimum for the zwitterionics, and a monotonic increase for the nonionics. Nevertheless, we note an overall increasing trend of Q with n. Recall that for these four series of surfactants the micelle aggregation number decreases with increasing headgroup size.[38,47,56,57] Since a less compact packing of the surfactant alkyl chains is expected as the aggregation number decreases, the microviscosity should have decreased upon increasing headgroup size. The observation of the reverse behavior suggests that other factors are at play in determining the observed changes of microviscosity.

A first factor is that discussed in explaining the increase of Q with m (preceding subsection), that is, the motion of the surfactant alkyl chains associated to the probe butterfly motion. However, the effect may now be less pronounced, and also, less regular because the motion to be considered here, that of the headgroups induced by the probe motion, takes place at the micelle surface to which the headgroups are tethered, via the motion of the alkyl chains.

A second factor is the average location of the probe in the micelles. The microviscosity reported by the probe may be larger when the probe is located closer to the micelle surface owing to the surfactant tethering to the surface which makes the local environment of the probe more rigid. The average location of P3P in the micelles of cationic and zwitterionic surfactants may be about the same in view of the identical nature of the headgroups (the zwitterionics also contain a quaternary ammonium headgroup). However, the probe location may be slightly different for the C_mE_n surfactants and also for the sugar surfactants than for the cationics. This factor is further discussed in the next subsection.

A last factor that may be at play, particularly in the case of the ethoxylated nonionic surfactants C_mE_n, is a partition of P3P between the outer shell of the micelle core and the micelle headgroup region which may be capable of solubilizing P3P. For the $C_{12}E_n$ surfactants, the volume of the headgroup region becomes larger than that of the core when the number of ethoxy groups n is larger than 3. The results in Figure 9 do show a monotonic increase of the microviscosity with the number n of ethoxy groups. Actually, Q still increases when going from $C_{12}E_{23}$ (surfactant **41**, ethoxy content = 86 wt %) to pure PEO

Aqueous Surfactant Micelles

J. Phys. Chem. B, Vol. 103, No. 43, 1999 **9123**

(compound **45**). However, results concerning the change of $E*$ with n do not support this assumption (see below in this subsection).

The values of $E*$ in Table 1 show little dependence on the headgroup size (see for instance the cationics **4** and **16−18**, the nonionics **38−41**, and the zwitterionics **54−57**), just like the values of Q. The $C_{12}C_nMe_2AB$ surfactants, where C_n represents a second alkyl chain of carbon number n (surfactants **2**, and **9−15**, with $n = 1−8$, including surfactant **14** which bears an OH group at the end of the second alkyl chain), also show very little dependence on n. In fact, in this series the micelles of surfactant **12** with $n = 5$ show the smallest values of both Q and $E*$. It is noteworthy that for this surfactant the second alkyl chain (pentyl) is most likely participating to the micelle core whereas for $n = 4$ the alkyl chain (butyl) may still be partitioned between the core and the water side of the micelle water interface. The mismatch between the length of the pentyl and dodecyl chains of surfactant **12** may cause an increased disorder in chain packing and, thus, a decrease of microviscosity at the solubilization site of P3P.

For the nonionic surfactants $C_{12}E_n$, $E*$ is nearly independent of the number n of ethoxy groups in the surfactant headgroup and the value of $E*$ is significantly smaller than for pure PEO (compound **45**). If P3P was partitioned between the micelle core and the headgroup region, as the possibility was considered above, $E*$ would have varied significantly with n for the $C_{12}E_n$ series. The constancy of $E*$ suggests that the amount of probe in the headgroup region is negligible for the ethoxylated surfactants investigated.

In surfactants **20−23** the size of the headgroup is increased by progressively substituting H atoms by CH_3 groups in the headgroup. This series shows a sharp drop in the value of $E*$ (and the ln Q vs $1/T$ plot becomes nonlinear) when introducing the first CH_3 in the headgroup (surfactant **21**). $E*$ increases back to nearly its value for DAC (compound **20**) and does not change further when substituting the last two H atoms by two CH_3 groups (surfactants **22** and **23**). We have presently no explanation for this behavior. However, one cannot exclude a small change of probe location with the number of methyl groups in the headgroup.

Effect of the Nature of the Surfactant Headgroup. This is probably the most difficult parameter to discuss. Indeed, differences in the nature of the surfactant headgroup most likely result in slight differences in the probe location in the micelles, and thus in the microviscosity reported by the probe. Aromatic probes such as pyrene or P3P are known to reside close to the micelle surface.[9,58,59] In cationic micelles this is further enhanced by the attractive interaction that is known to exist between aromatic compounds and ammonium headgroups.[58−60] This interaction is of essentially electrostatic nature and is due to the π-electron cloud that surrounds aromatic compounds. On this basis, the interaction between P3P and anionic surfactant headgroups is expected to be repulsive driving P3P somewhat deeper in the micelles. The systematically lower Q values characterizing anionic surfactant micelles with respect to cationic ones (factor of about 2 when comparing data at a given value of m and of the temperature; see Table 1) is thought to be essentially due to this difference of location. Indeed, the chain packing in the micelle core becomes increasingly disordered as one moves away from the core surface.[61,62] Thus the microviscosity sensed by the probe is expected to decrease if the probe is located farther away from the core surface.

Attractive interactions probably also exist between P3P and the positively charged quaternary ammonium headgroup of the

zwitterionic surfactants investigated. Attractive interaction may exist between aromatic compounds and POE headgroups since P3P is sparingly soluble in liquid PEO. This would result in values of Q larger than for anionic surfactant micelles, because the probe would be located closer to the micelle surface.

The $E*$ values for the anionic surfactant micelles are systematically lower than for the other surfactants, whether cationic, nonionic (ethoxylate or sugar headgroup) and zwitterionic. This may again be due to the difference in the P3P location between anionic micelles and the other types of micelles.

Above, the differences of microviscosity observed with surfactants of differing headgroups have been mostly attributed to differences of probe location in the micelles. It is clear however that a change of surfactant headgroup nature also involves a change of headgroup size and the preceding section showed that such a change can result in significant variations of microviscosity. Thus the effect of the headgroup nature on the micelle microviscosity is complex. Above we have attempted to separate as best as possible the effect of the nature of the headgroup from that of its size. Parameters other than the headgroup size may be associated to a change of headgroup nature but this study did not reveal them.

Effect of the Surfactant Chemical Structure. The microviscosity of micelles of surfactants of differing chemical structure can be compared at constant m, temperature, and nature of the headgroup, here the trimethylammonium bromide. The plots 1, 3, and 4 in Figure 7 show that the microviscosity increases in the sequence: C_mMe_3AB < bolaform < dimeric. It is noteworthy that the values of $E*$ for the conventional cationic surfactant **5**, the bolaform surfactant **6**, and the dimeric surfactant **61**, which all contain a hexadecyl chain, are characterized by the same value of $E*$, within the experimental error.

Effect of the Nature of the Counterion. The comparison of the plots 1 and 2 in Figure 7 shows that for cationics the microviscosity is smaller for the chloride surfactants C_mMe_3-AC than for the bromide surfactants C_mMe_3AB, irrespective of the value of m. Most likely a large part of this difference reflects the fact that micelles of quaternary ammonium surfactants of equal m values are always smaller with chloride than with bromide counterions.[39,63] This results in a looser packing and, thus, in lower Q values. The comparison of surfactants **3** and **5** to **23** and **24** shows a decrease of $E*$ by nearly 6 kJ/mol when substituting bromide by chloride counterions. This observation probably also relates to the more compact packing in bromide than in chloride micelles, like for the Q values.

The results for the anionic surfactants do not show a clear trend with the size of the counterion. Thus Q decreases slightly in going from potassium to rubidium decanoate (surfactants **26** and **27**), increases significantly in going from sodium to potassium dodecanoate (surfactants **28** and **29**), and decreases in going from sodium to hexylammonium dodecyl sulfate (surfactants **31** and **32**). Note that the 0.5 wt % solution of hexylammonium dodecyl sulfate was slightly bluish indicating the presence of vesicles. This is a common feature of the solutions of the so-called catanionic surfactants.[64,65] The solution of surfactant hexylammonium dodecyl sulfate remained bluish up to 50 °C, but clarified upon a 20 min sonication using a Branson 2200 sonicator.

Results for Specific Surfactants. *Microviscosity and Krafft Temperature.* The surfactants **5**, **8**, **20**, **21**, and **61** were investigated at temperatures that were in some instances below or very close to their Krafft temperature T_K which had the values 25 ± 0.5, 12.8 ± 0.3, 16.5 ± 0.5, 28.1 ± 0.5, and 41.0 ± 0.5 °C, respectively. These values correspond to the temperature

of clarification of the solutions determined by visual inspection, except for surfactant **8** where it was obtained by electrical conductivity measurements. The supercooled solutions of these surfactants, i.e., at $T < T_K$, remained clear and monophasic for a time much longer than that required for the measurements of τ_E and I_M/I_E. Nevertheless, surfactants **8**, **20**, and **21** were characterized by ln Q vs $1/T$ plots that were nonlinear in the T-range investigated, but not the surfactants **5** and **61**. A nonlinear ln Q vs $1/T$ plot was also obtained for the surfactant **32** that forms vesicles (see above). These differing results show that more studies are necessary in order to clarify the behavior of the microviscosity of micelles at the approach of the Krafft temperature.

The Q value for the bolaform surfactant **8** with $m = 22$ at 15 °C is very high (see Table 1). This surfactant is also characterized by a very large value of E^* and a highly nonlinear ln Q vs $1/T$ plot. Its Krafft temperature (12.8 °C at a concentration of 1.3 wt %) was below the lower temperature at which it was investigated. Thus for this surfactant the lowering of the temperature apparently induced an important increase of micelle microviscosity. Recall that an increase of microviscosity has been reported for lipid vesicles when going from above to below the melting temperature of the lipid chains.[22,66] A similar effect involving some change from a disordered conformation of the long $C_{22}H_{44}$ chain of this surfactant at high T to a somewhat more ordered conformation at low T may be responsible for the observed increase of Q.

The surfactant Triton X100 can be considered as the monomer of the surfactant oligomer Tyloxapol.[67] The microviscosity of TX100 micelles is seen to be much lower than that of Tyloxapol in the whole temperature range, a result similar to that found with cationic surfactant oligomers.[29] However, the E^* values for the two surfactants are nearly equal, a result different from that for cationic surfactant oligomers. Indeed, using previously reported Q values,[29] the E^* values for 12-3-12, 12-3-12-3-12, and 12-3-12-4-12-3-12 were found to be 70.3 ± 4, 66.5 ± 4, and 68.2 ± 4 kJ/mol, respectively, thus showing no effect of the degree of oligomerization of the surfactant. Nevertheless these values are much larger than for the corresponding surfactant monomer DTAB (surfactant **3**): 47.8 ± 2 kJ/mol. No explanation can be presented at this stage for this difference of behavior.

The microviscosity shows a very large increase in going from $C_{12}E_{23}$ (surfactant **41**, ethyleneoxide content of 86 wt %) to pure PEO (compound **45**). This increase is much larger than that expected from the smooth increase of Q with the ethyleneoxide content in the series of $C_{12}E_n$ surfactants. This behavior reflects the fact that in going from a $C_{12}E_n$ surfactant to pure PEO the surrounding of the probe undergoes a qualitative change, from somewhat hydrocarbon-like to pure PEO. It confirms that P3P is not partitioned between the micelle core and the PEO corona surrounding this core.

Last, we note that for given values of m and T the sugar surfactants **46**−**48** are characterized by much larger values of Q than all other surfactants. Thus at 15 °C and for $m = 8$, Q is around 800 ns for the sugar surfactants, while the values are around 400 ns for cationic, zwitterionic, and nonionic surfactants. The E^* values of sugar surfactants are also significantly larger than for other surfactants. A possible explanation for these differences is that hydrogen bonding may take place between sugar headgroups at the micelle surface. The H-bonded sugar surfactants then behave as pseudo surfactant oligomers, characterized by larger values of the microviscosity. Larger E^* would also result as the activation energy now includes a contribution for the breakage of the H-bonds.

Concluding Remarks and Summary

The microviscosity Q of the micelles of sixty surfactants differing by the alkyl chain length, nature of the headgroup (cationic, anionic, nonionic, and zwitterionic), size of the headgroup, structure of the surfactant (conventional, bolaform, dimeric), and temperature has been measured in aqueous solution using the viscosity-sensitive emission of the fluorescent probe 1,3-dipyrenylpropane. The activation energy of the microviscosity E^* was obtained from the variation of Q with temperature, in the range between 15 and 45 °C. The results showed an increase of Q and E^* with the surfactant alkyl chain carbon number. The increment of E^* per methylene group in the alkyl chain was found to depend little on the nature of the surfactant series investigated and to be only slightly larger than the increment of E^* for *n*-alkanes. This led to the conclusion that the large difference between the values of Q for an *n*-alkane and the micelle of a surfactant having the same alkyl chain length is essentially due to the tethering of the surfactant headgroup to the micelle surface. The values of Q and E^* were found to be significantly lower for anionic surfactant micelles than those for micelles of cationic, nonionic, and zwitterionic surfactants. The differences were attributed to a location of P3P somewhat closer to the surface of micelles of the latter surfactants, owing to the existence of attractive interactions between the probe and the surfactant headgroups. For the ethoxylated nonionic surfactants where the headgroup region is much more voluminous than the micelle core, the variations of Q and E^* with the number of ethoxy groups clearly show that the probe is nevertheless essentially located in the micelle core. The results concerning the effects of the surfactant chain length, size of the headgroup and counterion nature showed the importance of the packing of the surfactant alkyl chains in determining the micelle microviscosity. Last, the results showed that the microviscosity varies with the surfactant structure following the sequence: conventional surfactant < bolaform surfactant < dimeric surfactant.

References and Notes

(1) Wennerström, H.; Lindman, B. *Phys. Rep.* **1979**, *52*, 1.

(2) Lindman, B.; Wennerström, H. *Top. Curr. Chem.* **1980**, *87*, 3.

(3) Israelachvili, J.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525.

(4) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

(5) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

(6) Grätzel, M. In *Micellization and Microemulsion*; Mittal, K. L., Ed.; Plenum: New York, 1977; Vol. 2, p 531.

(7) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133.

(8) Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283.

(9) Zana, R. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed..; M. Dekker Inc.: New York, 1987; Chapter 5 and references therein.

(10) Shinitzky, M. *Isr. J. Chem.* **1974**, *12*, 879.

(11) Shinitzky, M.; Yuli, I. *Chem. Phys. Lipids* **1982**, *30*, 261.

(12) Shinitzky, M. In *Physical Methods on Biological Membranes and their Model Systems*; Plenum Publishing Corp.: New York, 1984; p 237.

(13) Zachariasse, K. A. *Chem. Phys. Lett.* **1978**, *57*, 429.

(14) Zachariasse, K. A.; Duveneck, G.; Busse, R. *J. Am. Chem. Soc.* **1984**, *106*, 1045.

(15) Infelta, P. P.; Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 190.

(16) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.

(17) Dowling, K. C.; Thomas, J. K. *Macromolecules* **1991**, *24*, 2341.

(18) Thomas, J. K. *J. Phys. Chem.* **1987**, *91*, 267.

(19) Lindman, B.; Södreman, O.; Wennerström, H. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed.; M. Dekker, Inc.: New York, 1987; Chapter 6.

(20) Taupin, C.; Dvolaitzky, M. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed.; M. Dekker, Inc.: New York, 1987; Chapter 7.

Aqueous Surfactant Micelles

J. Phys. Chem. B, Vol. 103, No. 43, 1999 **9125**

(21) Henderson, C. N.; Selinger, B. K.; Watkins, A. R. *J. Photochem.* **1981**, *16*, 215.

(22) Hare, F.; Amiell, J.; Lussan, C. *Biochim. Biophys. Acta* **1979**, *555*, 388 and references therein.

(23) Maiti, N.; Krishna, M.; Brotti, P.; Periasamy, N. *J. Phys. Chem. B.* **1997***, 101*, 11051.

(24) Weber, S.; Wolff, T.; von Bünau, G. *J. Colloid Interface Sci.* **1996**, *184*, 163.

(25) Huang, J. B.; Zhao, G.-X. *Colloid Polym. Sci.* **1996**, *274*, 747.

(26) Miyagishi, S.; Suzuki, H.; Asakawa, T. *Langmuir* **1996**, *12*, 2900.

(27) Miyagishi, S.; Asakawa, T.; Nishida, M. *J. Colloid Interface Sci.* **1987**, *115*, 199.

(28) Pistolis, G.; Malliaris, A. *Langmuir* **1997**, *13*, 1457.

(29) Zana, R.; In, M.; Lévy, H.; Duportail, G. *Langmuir* **1997**, *13*, 5552.

(30) Lianos, P.; Lang, J.; Zana, R. *J. Colloid Interface Sci.* **1983**, *91*, 276.

(31) Turley, W. D.; Offen, H. W. *J. Phys. Chem.* **1985**, *89*, 2933; **1986**, *90*, 1967.

(32) Evertsson, H.; Nilsson, S. *Macromolecules* **1997**, *30*, 2377.

(33) Zana, R. *J. Colloid Interface Sci.* **1998**, *78*, 330.

(34) Yiv, S.; Zana, R. *J. Colloid Interface Sci.* **1980**, *77*, 449.

(35) Ikeda, K.; Yasuda, M.; Ishikawa, M.; Esumi, K.; Meguro, K.; Binana-Limbélé, W.; Zana, R. *Colloid Polym. Sci.* **1989**, *267*, 825.

(36) Zana, R.; Yiv, S.; Kale, K. M. *J. Colloid Interface Sci.* **1980**, *77*, 456.

(37) Zana, R.; Lévy, H. *Colloids Surf. A.* **1997**, *127*, 229.

(38) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1985**, *89*, 2709.

(39) Malliaris, A.; Lang, J.; Zana, R. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 109.

(40) Jada, A.; Lang, J.; Zana, R. *J. Phys. Chem.* **1990**, *94*, 381.

(41) Graber, E.; Lang, J.; Zana, R. *Kolloid Z. Z. Polym.* **1970**, *238*, 470.

(42) This surfactant was prepared according to the method reported by Shinoda, K. *J. Phys. Chem.* **1955**, *59*, 432.

(43) Alami, E.; Kamenka, N.; Raharimihamina, A.; Zana, R. *J. Colloid Interface Sci.* **1993**, *158*, 342.

(44) Aoudia, M.; Zana, R. *J. Colloid Interface Sci.* **1998**, *206*, 158.

(45) Frindi, M.; Michels, B.; Zana, R. J. *Phys. Chem.* **1992**, *96*, 8137.

(46) Frindi, M.; Michels, B.; Zana, R. *J. Phys. Chem.* **1994**, *98*, 6607.

(47) Kamenka, N.; Chevalier, Y.; Zana, R. *Langmuir* **1995**, *11*, 3351.

(48) Winnik, F. M.; Winnik, M. A.; Ringsdorf, H.; Venzmer, J. *J. Phys. Chem.* **1991**, *95*, 2583.

(49) Kabanov, A. V.; Nazarova, I. R.; Astafieva, I. V.; Batrakova, E. V.; Alakhov, V. Y.; Yaroslavov, A. A.; Kabanov, V. A. *Macromolecules* **1995**, *28*, 2303.

(50) Miyagishi, S.; Kurimoto, H.; Ishihara, Y.; Asakawa, T. *Bull Chem. Soc. Jpn.* **1994**, *67*, 2398.

(51) Miyagishi, S.; Kurimoto, H.; Asakawa, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 135.

(52) Miyagishi, S.; Kurimoto, H.; Asakawa, T. *Langmuir* **1995**, *11*, 2951.

(53) Miyagishi, S.; Akasohu, W.; Hashimoto, T.; Asakawa, T. *J. Colloid Interface Sci.* **1996**, *184*, 527.

(54) Huang, J. B.; Zhao, G.-X. *Colloids Polym.* **1996**, *274*, 747.

(55) Handbook of Chemistry and Physics, 53rd ed.; CRC Press: Cleveland, 1972; p F37.

(56) Zana, R.; Weill, C. *J. Phys. Lett.* **1985**, *46*, L-953.

(57) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* **1981**, *84*, 100.

(58) Bacaloglu, R.; Bunton, C.; Cerichelli, G.; Ortega, F. *J. Phys. Chem.* **1989**, *93*, 1490.

(59) Bacaloglu, R.; Bunton, C.; Ortega, F. *J. Phys. Chem.* **1989**, *93*, 1497.

(60) Lianos, P.; Viriot, M.-L.; Zana R. *J. Phys. Chem.* **1984**, *88*, 1098.

(61) Walderhaug, H.; Sodreman, O.; Stilbs, P. *J. Phys. Chem.* **1984**, *88*, 1655.

(62) Néry, H.; Sodreman, O.; Canet, D.; Walderhaug, H.; Lindman, B. *J. Phys. Chem.* **1986**, *90*, 5802.

(63) Alargova, R. G.; Kochijashky, I. I.; Zana, R. *Langmuir* **1998**, *14*, 1575.

(64) Marques, E.; Regev, O.; Khan, A.; Miguel, M.; Lindman, B. *J. Phys. Chem. B* **1998**, *102*, 6746.

(65) Iampietro, D.; Brasher, L.; Kaler, E.; Stradner, A.; Glatter, O. *J. Phys. Chem. B* **1998**, *102*, 3105.

(66) Zachariasse, K.; Kühnle, W.; Weller, A. *Chem. Phys. Lett.* **1980**, *73*, 6.

(67) Regev, O.; Zana, R. *J. Colloid Interface Sci.* **1999**, *210*, 8 and references therein.