Investigation of SDS, DTAB and CTAB micelle microviscosities by Electron Spin Resonance.

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Abstract

Electron spin resonance spectroscopy (ESR) of the nitroxide labelled fatty acid probes (5-, 16-doxyl stearic acid) was used to monitor the micelle microviscosity of three surfactants at various concentrations in aqueous solution: sodium dodecyl sulphate (SDS), dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB). At low surfactant concentration, there is no micelle, the ESR probe is dissolved in water/surfactant homogeneous phase and gives his microviscosity. At higher surfactant concentration, an abrupt increase in microviscosity indicates the apparition of micelles and, the solubilization of the probes in micelles. The microviscosity of the three surfactants, in a large surfactant range, was obtained as well as the critical micelle concentration (CMC). The microviscosity increased slightly with the increase in surfactant concentration. Phosphate buffer lowered the CMC value and generally increased the microviscosity.

Key words: ESR; micelle; microviscosity.

Introduction

Several methods for studying micellization phenomenon and self-aggregate behaviour of amphiphiles molecules in aqueous and non-aqueous media have been reported in the literature. Surface tension [1], electrical conductivity [2], light scattering [3] [4], and various spectroscopic technique [5-7] have been used to measure critical micelle concentration (CMC), aggregate size, and aggregation number of surfactants. Local parameters like micropolarity and microviscosity were studied in order to better understand micellar self-assembly. A considerable effort has been made in the past to measure microviscosity of various self-assemblies formed by synthetic and natural lipids [8]. Among various methods, fluorescence [9], electron spin resonance (ESR) [7], and nuclear magnetic resonance (NMR) [10] techniques have been widely used. Most of the studies report a relative information about the microviscosity of the explored solution [11] or an absolute value of the microviscosity but only at a fixed surfactant concentration [5,12,13].

The relative anisotropy observed in an ESR spectrum is directly related to the rotational mobility of the probe, and can be correlated with the probe's microenvironment. The change in probe mobility allows to study the formation of aggregates in solution and often yields useful information on the aggregate structure [7]. In particular, nitroxide labeled fatty acid probes (n-doxyl stearic acid) have been useful in determining these parameters within micelles [7]. Absolute values of microviscosity can be obtained after prior calibration of the ESR spectra of nitroxide probes in solvent mixtures of known viscosities [14]. In these experiments, the microviscosity is defined as the homogenous solution viscosity, which results in the same spectrum as that in the microenvironment [12,14]. In the present work, using the ESR technique and n-doxyl stearic acid spin probes, the microviscosity values in a large concentration range and the CMC of sodium dodecyl sulphate (SDS), dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB) surfactants were determined both in unbuffered and phosphate buffer (1/15 M, pH 7) aqueous solutions.

2. Materials and methods

2.1. Chemicals

SDS was purchased from Janssen Chimica (Belgium), DTAB and CTAB from Sigma Chemical Company (Belgium). They were used as received. Stearic acid spin probes (n-DSA, n = 5, 16); 2-(3-carboxypropyl)-4,4-dimethyl-2-tridecyl-3-oxazolidinyloxy (5-DSA); 2-(14-carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidinyloxy (16-DSA) from Aldrich (Belgium) were with analytical grade and used without further purification. Water was laboratory deionized and distilled. Phosphate buffer stock solution (Na_2HPO_4-KH_2PO_4, Ridel-de Haën, Belgium) was also laboratory prepared. Dilutions were calculated to obtain a final 1/15 M concentration (pH 7.0) in all surfactant solutions.

2.2. Instrumentation and procedure

Stock solutions (5 10^{-1} M) of surfactants were prepared in distilled water or in phosphate buffer solution. The pH was measured using a handheld pH-meter (WTW, model PH 330i, Germany). These stock solutions were diluted in order to obtain samples at concentrations ranging from 2 10^{-5} to 5 10^{-1} M of surfactant. Spin-labeled stearic acids n-DSA solubilised in ethanol were added to each surfactant sample. In all studies, the probe-to-surfactant molar concentration ratio did not exceed 1/100 and the added ethanol quantity was less than 1/100 of solution volume.

The surface tension experiments were performed using pendant drop shape analysis technique (Cam200, KSV Instruments, USA) [15]. Standard deviations were calculated from eight measurements.

The ESR spectra were recorded at 9.56 GHz using a Bruker ESR 300E spectrometer (Bruker, Germany). All measurements were made at room temperature and using an aqueous flat cell. Spectra were recorded with an 80 G scan range at 20 mW microwave power and 2 G modulation amplitude. All samples were used immediately after preparation and without deoxygenation. It is known that nitroxide probes interact with oxygen dissolved in solution inducing an ESR line broadening. This

effect is estimated to be 100 mG in physiological solution in equilibrium with air [16]. Regarding the ESR line width ($\Delta\omega$) of n-DSA in aqueous media ($\Delta\omega$ > 1 G), this broadening effect can be neglected. Baglioni et al have been mentioned in a similar study that this broadening effect is almost negligible in water solution [17]. The mobility of n-DSA in the explored medium was quantified by correlation time (τ_c) as described elsewhere [7] in the case of weakly to moderately immobilized probes (τ_c<3 10^{-9} s) [18]. Previously established standard curves of microviscosity versus correlation time [14] were used to convert measured correlation time into micelle microviscosity. The microviscosity standard deviation was estimated to 7.5 %. This value was calculated from five measurements at 0.1 M SDS concentration.

3. Results and discussion

3.1. Surface tension experiments

When the surface tension of solutions with increasing concentration of surfactant is measured, the surface tension vs. surfactant concentration plots show two straight lines, one with a steep negative slope and the other with a slightly decreasing one (Fig. 1). The line with a steep linear decrease corresponds to the concentration range below the CMC: only monomers of surfactant exist at the solution surface. At higher concentrations, the solution surface becomes crowded with surfactant. Any further addition of surfactant must arrange as micelles and no further change in surface tension is detected. The intersection of linear decline line and the baseline of minimal surface tension (Fig. 1) was taken as the CMC value of surfactant [1]. The measured value of surface tension in distilled water without surfactant is 72 mN/m, which is in agreement with value given in literature [19]. This value decreases linearly with surfactant concentration until reaching a minimal value which is 35 mN/m for SDS (Fig. 1), 37 mN/m for DTAB (data not shown) and 36 mN/m for CTAB (data not shown). These values proved to be consistent with values obtained by others [1]. CMC values for SDS, DTAB and CTAB in distilled water and in phosphate buffer solution (1/15 M, pH 7.0) are presented in Table 1. These CMC values are in good agreement with values reported in literature (Table 1). The CMC value is clearly lower in phosphate buffer as a result of the well known electrolyte effect on micelle formation [2,3,20]. The electrolyte neutralizes the charge at the micelle surface, reduces the thickness of the ionic layer around the surfactant ionic heads and, therefore, the electrostatic repulsions between them, helping in this way the micellization process.

Some spectroscopic probes are able to modify the CMC value of surfactants [2,17]. (This results from interactions between the surfactant monomers and the probes, which alter the micellization process. Therefore, the influence of ethanol [21] and n-DSA probes on surface tension and on CMC values was investigated. The addition of n-DSA primarily dissolved in ethanol decreases clearly the surface tension below the CMC (Fig. 1), but does not seem to affect nor the CMC values nor the surface tension above the CMC (Fig. 1 and Table 1). The spin probe-to-surfactant concentration ratio,

calculated at CMC concentration, was less than 1/100. The added ethanol volume (≤ 5 μl) was lower than 1/100 of the surfactant solution volume (500 μl) and decreased slightly the surface tension from 72 to 69 mN/m.

3.2. ESR study of SDS aqueous solutions

Electron spin resonance is currently used to investigate the microenvironment of nitroxide spin probe in micellar systems by measuring the nitrogen-coupling constant and ESR spectra line width [18]. The line width is very sensitive to the rotational and lateral diffusion of the spin probes, which in turn is affected by viscosity and temperature of the local microenvironment [18]. Thus, the relative anisotropy observed in an ESR spectrum is directly related to the probe rotational mobility, a term that can be correlated with the microviscosity of the probe environment [12]. This correlation allows to measure the local microviscosity inside micelles by using spin labelled stearic acids (5- and 16-DSA) and standard curves of microviscosity which were established in a previous work [14]. These curves relate the microviscosity of the probe microenvironment to the correlation time of the spin probe ($\tau_c < 3\ 10^{-9}$ s).

Fig. 2 shows the EPR spectrum of 5-DSA in distilled water, 2.0 10^{-3} M and 6.0 10^{-2} M SDS aqueous solution, respectively. The correlation times of 5-DSA measured in the three solutions were 1.63 10^{-10}, 1.63 10^{-10}, and 10.79 10^{-10} s, respectively. These correlation time values correspond to a local microviscosity of 0.3, 0.3, and 14.79 cP, respectively. Each line constituting the three spectra of Fig. 2 was found symmetric to their horizontal central line and did not present any distortion. It indicates that the probe experiments only one medium. Indeed, the lines become asymmetric and highly distorted when probes coexist in water and micelles [17,22,23]. At low SDS concentration, there is no micelle and the probe is dissolved in water only, and consequently sensing the water viscosity, while, at high SDS concentration, micelles appear and all probes are solubilized in the micelles. Fig. 3 shows the microviscosity sensed by the probe in SDS solutions as a function of surfactant

concentration. The microviscosity plots show three distinct regions. A first one (I) characterized by symmetric and not distorted ESR spectrum and by low microviscosity values (0.3 cP) was obtained for a concentration of SDS up to 5 10^{-3} M (Fig. 3.a). The second region (II) can be identified by a lack of microviscosity values on the plot (Fig. 3. a; 5 10^{-3} < [SDS] < 10^{-2} M). In this surfactant concentration range, ESR spectra were highly distorted, and consequently, spectral parameters and microviscosity were inaccessible. Spectrum distortion results from the superposition of three different absorptions signals: the bulk water spectrum; the micelle spectrum and a broad single line underlying a spin-exchange-narrowed signal which can be attributed to micelles containing several spin-probe molecules per micelle. This phenomenon was previously reported in several colloidal systems [17,23]. In this region surface tension continues to decrease (Fig. 1). The third region (III) is considered as post CMC surfactant concentration region (Fig. 3. a; [SDS] >10^{-2} M). The ESR spectrum is again symmetric and did not present any distortion. The microviscosity increased abruptly to about 12 cP. The increase of microviscosity is a clear indication of probe motion restriction, and this is often taken as proof of micelle onset when observed in surfactant solutions [24]. When the SDS concentration became larger than its CMC value, probe molecule was transferred from water into micelle and locates itself in the hydrocarbon nucleus of the micelle [25]. The n-DSA chain was shown to orient approximately in the direction of the micelle surface normal [26,27]. The obtained microviscosity values agree well with the ones found by others in water solution and at different SDS concentration (16.33 cP at 4 10-2 M [5]; 19 cP at 0.1 and 4 10-2 M [28] [29]) using fluorescence probe. From the data of Fig. 3, a critical micelle concentration is taken as the middle of the segment relating the point of the highest surfactant concentration in the low viscosity region and the point of the lowest surfactant concentration in micelle region. CMC values for SDS obtained by this way, in unbuffered water and in phosphate buffer are displayed in Table 1. These values agreed well with those obtained by surface tension measurement and with those given in literature for surfactant-aqueous solutions without DSA probes (Table 1).

5-DSA and 16-DSA give very similar values of micelle microviscosity (Fig. 3), at any surfactant concentration, both in unbuffered water and in phosphate buffer. This can be explained by the fact that the end of the DSA chain may squeeze up due to vertical fluctuations. Consequently 16-DSA explores sensibly the same region than does 5-DSA [30-32]. Between 10 and 60 mM (Fig. 3a), a trend of slight increase in microviscosity is observed. This can be explained by the fact that water intercalated between the surfactant head groups is progressively eliminated with the increase of the SDS concentration [33,34]. Consequently, micelle head groups region become progressively more compact and more viscous. The progressive increase of microviscosity above to 10^{-1} M SDS in unbuffered water could indicate a change in micelle structure. The formation of cylindrical aggregates has been observed in this SDS concentration range [27].

When SDS is dissolved in phosphate buffer, the microviscosity detected in the region of SDS concentration range above CMC (Fig. 3 b) is higher than in pure water (Fig. 3 a). In fact, the salts of phosphate buffer ionise in solution and the sodium and potassium ions tend to condense the counterions onto the micelle surface. This results in a decrease of the ionization degree and an increase in the aggregation number [2]. Also, the decrease of electrostatic repulsive force between polar head makes the micelles more compact and less hydrated [3]. This should increase the microviscosity.

3.3. ESR study of CTAB and DTAB aqueous solutions

Critical micelle concentration and micelle microviscosity for two cationic surfactants, DTAB and CTAB, have also been studied through ESR technique by employing 5- and 16-DSA as spin probes. Fig. 4 shows the variation of microviscosity sensed by the two spin probes in DTAB and CTAB aqueous solution, as function of detergent concentration. These plots of microviscosity show the same three regions observed in the case of SDS: the region (Ⅰ) of low microviscosity where the probe moves freely in the bulk solution, the transition region (Ⅱ) where the determination of microviscosity was not possible, and finally the third region (Ⅲ) where the probe is inside the

micelles. It should be noted that the transition region extended over a larger concentration range than in the case of SDS (Figs 3 and 4). This extending of the transition region makes less accurate the determination of the CMC values. Consequently, the CMC values determined from microviscosity plots showed to be somewhat different than those found by surface tension method, especially for DTAB (Table 1). In the low surfactant concentration region, the spectra of 5-DSA and 16-DSA in CTAB, DTAB and SDS solutions present a very similar shape. Very close correlation times were obtained, and therefore the microviscosity values were very similar.

Likewise in SDS, microviscosity values of DTAB in unbuffered water (Fig. 4a) and in phosphate buffer solution (Fig. 4b), obtained with 5- and 16-DSA are very similar. It should be pointed out that DTAB and SDS molecules present the same hydrocarbon chain length (12 carbons). This reinforces the hypothesis that due to squeezing up phenomenon of the DSA chain (16 carbons), 16-DSA explore sensibly the same micellar region as does 5-DSA. In water, measured microviscosity in DTAB micelles is about 24 cP, which is higher than the 12 cP value found in SDS micelles. Comparing Fig. 4a, and 4b, phosphate buffer has a low effect on DTAB micelle microviscosity, although the increase in microviscosity with surfactant concentration is steeper in phosphate buffer. Fig. 4c and 4d show the microviscosity plots of CTAB dissolved in unbuffered water and in phosphate buffer. In this case, CTAB and n-DSA have the same hydrocarbon chain length (16 carbons). This may facilitate a deep localization of the nitroxyl group of 16-DSA in micellar nucleus core, even if 16-DSA undergoes a squeezing phenomenon. In unbuffered water (Fig. 4c) the microviscosity of the deep micelle region explored by 16-DSA appears to be somewhat lower than that of the outer region experienced by 5-DSA

5-DSA and 16-DSA experience for CTAB a higher microviscosity values (Fig. 4c, 4d) than those measured for DTAB (Fig. 4a, 4b), both in unbuffered water and in phosphate buffer. This may indicate that CTAB form a micelle structure more organised and less hydrated than does DTAB. Tedeschi et al. [35] have determined by using ESR technique that CTAB micelles have a highly organised surface structure comparing to micelles of alkyltrimethylammonium bromides with shorter

chain tails. They suggest that it indicates a different micellar structure. CTAB micelles tend to be rod-like rather than spherical.

When CTAB is dissolved in phosphate buffer, CMC value is shifted to lower values thanks to the electrolyte action, which boosts the micellization phenomenon. 5-DSA gives a larger micelle microviscosity than does 16-DSA (Fig. 4d). This could result from the increase in the aggregation number and the lower hydratation of the micelle surface [3,11]. Moreover, 16-DSA still probes the same microviscosity as that probed in water medium. This could be easily explained if micelles are cylindrical or rod-like. Indeed, in this kind of configuration, surfactants chains are directed towards the central micelles line. Therefore, any supplementary surfactant chain can be inserted without any significant increase of the compacting degree of micelle core. In contrast, if micelle has a spherical configuration, all hydrocarbon chains of surfactant molecules will be directed towards the same central point and any supplementary chain reduces the free space inside micelle and consequently should increase local viscosity.

Microviscosity values DTAB and CTAB micelles, obtained by our ESR method, are in concordance with those obtained by other techniques. By using a fluorescence technique, Shinitzky et al., [9] have reported a value of microviscosity of CTAB between 19 and 30 cP in water and at 20 mM as a surfactant concentration, Roy et al., [5] have obtained 13.22 and 17.77 cP for the microviscosity of DTAB and CTAB in water and at a concentration of surfactant of 81 and 5 mM, respectively.

4. Conclusion

In the present work the microviscosity of three surfactants, SDS, DTAB and CTAB, has been investigated by the use of ESR spin probing technique, and in two different aqueous medium, water and phosphate buffer (pH 7, 1/15 M). Microviscosity values were obtained throughout a wide surfactant concentration range (0 – 0.5 M). According to the obtained results, self-aggregation behaviour seems to be more marked and cooperative for CTAB than for SDS and DTAB thanks to the higher number of carbon atoms in CTAB tail. It is interesting to note that surfactants CMC values can also be estimated from the microviscosity plots.

References

[1] F. Hernainz, A. Caro, Variation of surface tension in aqueous solutions of sodium dodecyl sulfate in the flotation bath, Colloids Surf., A 196 (2002) 19-24.
[2] E. Fuguet, C. Rafols, M. Rosés, E. Bosch, Critical micelle concentration of surfactants in aqueous buffered and unbuffered systems, Anal. Chim. Acta 548 (2005) 95-100.
[3] C. Thevenot, B. Grassl, G. Bastiat, W. Binana, Aggregation number and critical micellar concentration of surfactant determined by time-dependent static light scattering (TDSLS) and conductivity, Colloids Surf., A 252 (2005) 105-111.
[4] H. Reerink, Micelle formation of sodium and potassium (tripentylmethyl) benzenesulfonate in n-heptane, J. Colloid Sci. 20 (1965) 217-230.
[5] S. Roy, A. Mohanty, J. Dey, Microviscosity of bilayer membranes of some N-acylamino acid surfactants determined by fluorescence probe method, Chem. Phys. Lett. 414 (2005) 23-27.
[6] P. Somasundaran, N.J. Turro, P. Chandar, Fluorescence probing of microfluidity of surfactant layers at the solid-liquid interface, Colloids Surf. 20 (1986) 145-150.
[7] F. Li, G-Z. Li, H-Q. Wang, Q-J. Xue, Studies on cetyltrimethylammonium bromide (CTAB) micellar solution and CTAB reversed microemulsion by ESR and 2H NMR, Colloids Surf., A 127 (1997) 89-96.
[8] M. Shigeyoshi, S. Hiroshi, A. Tsuyoshi, Microviscosity and Aggregation Number of Potassium N-Acylalaninate Micelles in Potassium Chloride Solution, Langmuir 12 (1996) 2900-2905.
[9] M. Shinitzky, A.C. Dianoux, C. Itler, G. Weber, Microviscosity and order in the hydrocarbon region of micelles and membranes determined with fluorescent probes. I. Synthetic micelles, Biochemistry 10 (1971) 2106-2113.
[10] O. Lindman, O. Södreman, H. Wennerström, Surfactant Solutions, New Methods of Investigation, Marcel Dekker, New York, 1987.
[11] A.M. Tedeschi, L. Franco, M. Ruzzi, L. Paduano, C. Corvaja, G. D'Errico, Micellar aggregation of alkyltrimethylammonium bromide surfactants studied by electron paramagnetic resonance of an anionic nitroxide, Phys. Chem. Chem. Phys. 5 (2003) 4204-4209.
[12] P. Chandar, P. Somasundaran, K.C. Waterman, N.J. Turro, Variation in nitroxide probe chain flexibility within sodium dodecyl sulfate hemimicelles, J. Phys. Chem., B 91 (1987) 148-150.
[13] P. Lianos, L. Jacques, S. Claude, Z. Raoul, Fluorescence probe study of oil-in-water microemulsions. 1. Effect of pentanol and dodecane or toluene on some properties of sodium dodecyl sulfate micelles, J. Phys. Chem. 86 (1982) 1019-1025.
[14] M.A. Bahri, B.J. Heyne, P. Hans, A.E. Seret, A.A. Mouithys-Mickalad, M.B. Hoebeke, Quantification of lipid bilayer effective microviscosity and fluidity effect induced by propofol, Biophys. Chem. 114 (2005) 53-61.
[15] J.M. Andreas, E.A. Hauser, W.B. Tucker, Boundary tension by pendant drops, J. Phys. Chem. 42 (1938) 1001-1019.
[16] H.M. Swartz, and J.F. Glockner, in S.S.E. Gareth R. Eaton, Keiichi Ohno (Ed.), EPR Imaging and In Vivo EPR. CRC Press, Inc, Broca Raton, FL, 1991, p. 261.
[17] P. Baglioni, E. Ferroni, G. Martini, M.F. Ottaviani, Micellar solutions of sulfate surfactants studied by ESR of nitroxide radicals. 2. Use of C8, C12, and C16 derivatives of piperidinyl-1-oxy, J. Phys. Chem. 88 (1984) 5107.

[18] N. Deo, P. Somasundaran, Electron spin resonance study of phosphatidyl choline vesicles using 5-doxyl stearic acid, Colloids Surf., B 25 (2002) 225-232.
[19] P-G. de Gennes, F. Brochard-Wyart, D. Quéré, Gouttes, bulles, perles et ondes, Belin, Paris, 2002.
[20] R. De Paula, A.E. da Hora Machado, J.A. de Miranda, 3-Benzoxazol-2-yl-7-(N,N-diethylamino)-chromen-2-one as a fluorescence probe for the investigation of micellar microenvironments, J. Photochem. Photobiol., A 165 (2004) 109-114.
[21] R. Zana, Aqueous surfactant-alcohol systems: a review, Adv. Colloid Interface Sci. 57 (1995) 1-64.
[22] J. Oakes, Magnetic resonance studies in aqueous systems. 1. Solubilization of spin probes by micellar solution, Mol. Chem. Phys. 68 (1972) 1464-1471.
[23] M.F. Ottaviani, P. Baglioni, G. Martini, Micellar solutions of sulfate surfactants studied by electron spin resonance of nitroxide radicals. 1. Use of neutral and positively charged spin probes, J. Phys. Chem. B 87 (1983) 3146-3153.
[24] P. Baglioni, M.F. Ottaviani, G. Martini, Micellar solutions of sulfate surfactants studied by ESR of nitroxide radicals. 3. Effect of added electrolytes, J. Phys. Chem. 90 (1986) 5878-5882.
[25] P. Baglioni, E. Rivara-Minten, L. Kevan, Electron spin resonance and electron spin echo modulation of n-doxylstearic acid and N,N,N',N'-tetramethylbenzidine photoionization in sodium versus lithium dodecylsulfate micellar solutions: effect of 15-crown-5 and 18-crown-6 ether addition, J. Phys. Chem. 92 (1988) 4726-4730.
[26] B.G. Dzikovski, V.A. Livshits, EPR spin probe study of molecular ordering and dynamics in monolayers at oil/water interfaces, Phys. Chem. Chem. Phys. 5 (2003) 5271-5278.
[27] F. Li, G-Z. Li, L. Zhai, L-Q. Zheng, H-Li. Wang, Fluorescence probe studies on the second critical micelle concentration of several kinds of surfactants, J. Dispersion Sc. Technol. 15 (1994) 705-710.
[28] K.A. Zachariasse, Intramolecular excimer formation with diarylalkanes as a microfluidity probe for sodium dodecyl sulfate micelles, Chem. Phys. Lett. 57 (1978) 429-432.
[29] W.D. Turley, H.W. Offen, Micellar microfluidities at high pressures, J. Phys. Chem. 89 (1985) 2933-2937.
[30] J.B. Feix, C.A. Popp, S.D. Venkataramu, A.H. Beth, J.H. Park, J.S. Hyde, An electron-electron double-resonance study of interactions between [14N]- and [15N]stearic acid spin-label pairs: lateral diffusion and vertical fluctuations in dimyristoylphosphatidylcholine, Biochemistry 23 (1984) 2293-2299.
[31] M. Hoebeke, A. Seret, J. Piette, A. Van de Vorst, Destruction of stearic acid nitroxyl radicals mediated by photoexcited merocyanine 540 in liposomal and micellar systems, Biochemistry 32 (1993) 2730-2736.
[32] M. Hoebeke, M. Enescu, L. Lindqvist, Quenching of merocyanine 540 triplet state by nitroxyl radicals in liposomal systems: a laser flash photolysis study, J. Photochem. Photobiol. B: Biol. 22 (1994) 229-233.
[33] A. Seret, A. Van de Vorst, Solubility properties of Eosin Y and Rose Bengal triplet state in sodium dodecyl sulfate micellar solutions, J. Phys. Chem. 94 (1990) 5293-5299.
[34] J. Georges, J.W. Chen, Microemulsions studies: correlation between viscosity, electrical conductivity and electrochemical and fluorescent probe measurements, Colloid. Polym. Sci. 264 (1986) 896-902.

[35] A.M. Tedeschi, G. D'Errico, E. Busi, R. Basosi, V. Barone, Micellar aggregation of sulfonate surfactants studied by electron paramagnetic resonance of a cationic nitroxide: an experimental and computational approach, Phys. Chem. Chem. Phys. 4 (2002) 2180-2188.
[36] A. Seret, E. Gandin, A. Van de Vorst, Flash photolysis of eosin in aqueous micellar dispersions, Chem. Phys. Lett. 135 (1987) 427-431.

Figure captions:

Fig. 1. Surface tension vs. molar concentration of sodium dodecyl sulfate (SDS). (a) In water; (b) in phosphate buffer (1/15 M; pH 7.0).

Fig. 2. ESR spectra of 5-DSA. (a) In water; (b) in 2 10^{-3} M SDS aqueous solution; and (c) in 6 10^{-2} M SDS aqueous solution (signal intensity decrease results from line broadening).

Fig. 3. Viscosity vs. SDS concentration as determined by 5- and 16-DSA. (a) In water, and (b) in phosphate buffer (1/15 M; pH 7.0); regions (Ⅰ), (Ⅱ), (Ⅲ) see text for further details.

Fig. 4. Viscosity vs. surfactant concentration as determined by 5- and 16-DSA. (a) DTAB in water; (b) DTAB in phosphate buffer (1/15 M; pH 7.0); (c) CTAB in water; and (d) CTAB in phosphate buffer (1/15 M; pH 7.0); regions (Ⅰ), (Ⅱ), (Ⅲ) see text for further details.

Table 1. Microviscosity and critical micelle concentration (CMC) values of SDS, DTAB and CTAB in aqueous solution.

	η (cP) (0.04 M of surfactant)	η (cP) (0.1 M of surfactant)	CMC* (mM)	CMC** (mM)	CMC*** (mM)
SDS in water	-	-	-	9	8 [36], 8.5 [7]
SDS in water (5 DSA)	12.8	12.3	7	9	-
SDS in water (16 DSA)	11.2	14.6	7	8	-
SDS in phosphate buffer	-	-	-	2	1.99 [2] (Phosphate buffer, 0.05 M, pH 7)
SDS in phosphate buffer (5 DSA)	23.9	23.5	3	2	
SDS in phosphate buffer (16 DSA)	25.3	23.7	3	2	
DTAB in water	-	-	-	14	14 [11]
DTAB in water (5 DSA)	23.4	23.7	7	14	-
DTAB in water (16 DSA)	22.9	24.7	7	11	-
DTAB in phosphate buffer	-	-	-	11	-
DTAB in phosphate buffer (5 DSA)	21.2	24.6	6	10	-
DTAB in phosphate buffer (16 DSA)	18.3	20.3	5	10	-
CTAB in water	-	-	-	0.8	1.1 [11]
CTAB in water (5DSA)	30.2	28.9	0.4	0.8	-
CTAB in water (16DSA)	28.8	32.7	0.4	-	-
CTAB in phosphate buffer	-	-	-	0.2	-
CTAB in phosphate buffer (5 DSA)	35.5	44.6	0.2	0.2	-
CTAB in phosphate buffer (16 DSA)	27.7	30.8	0.35	0.2	-

* Obtained by ESR method
** Obtained by surface tension method
*** From literature

Fig. 1.

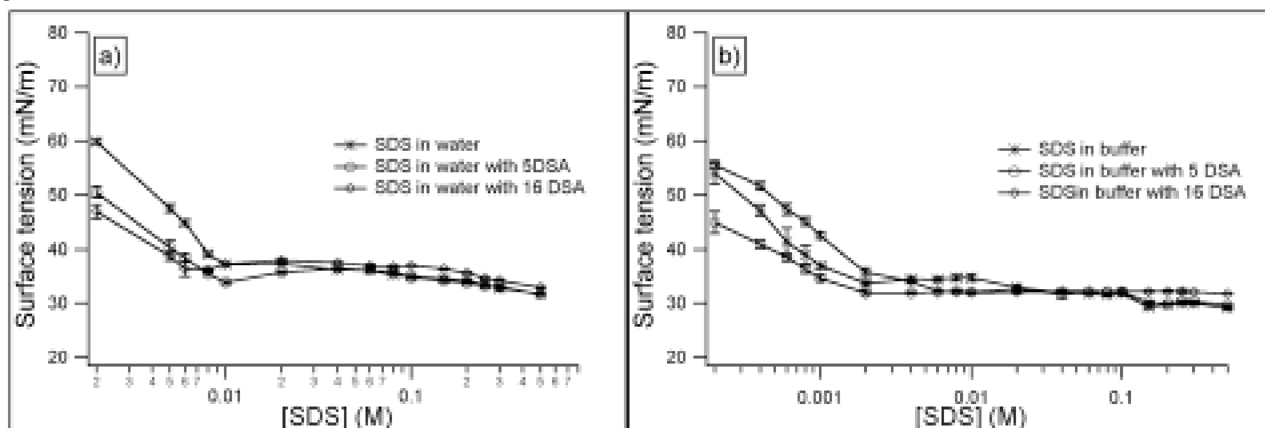

Fig. 2.

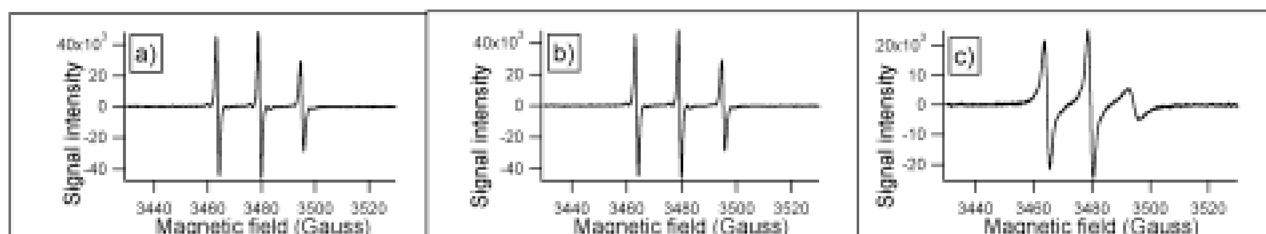

Fig. 3

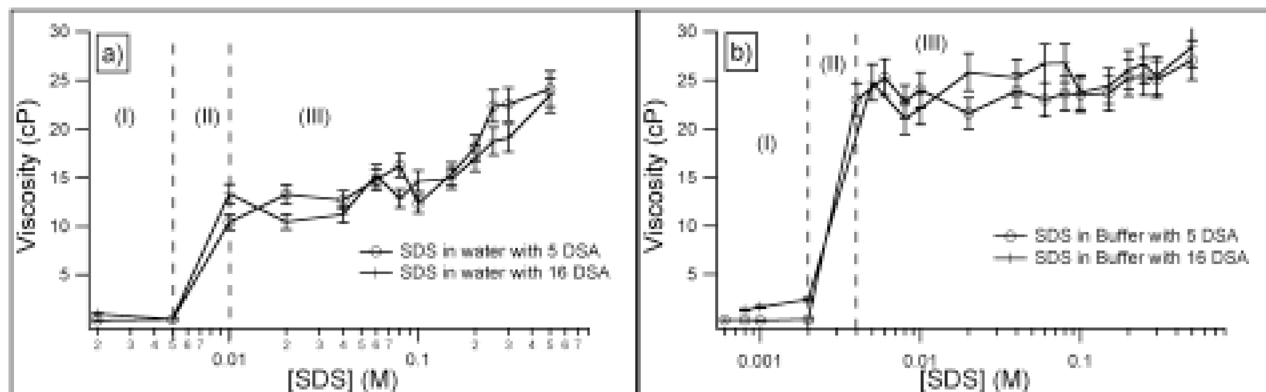

Fig. 4.