alcohol surfactants in near-critical and supercritical alkane continuous phases. For these systems the micelle or droplet diffusion coefficient is strongly pressure dependent, increasing by approximately 30% in the first 100 bar above the clearing point. We attribute this rapid increase primarily to a decrease in dropletdroplet attractive forces. Any contribution due to surfactant deaggregation as pressure increases is small, and available evidence indicates that actual droplet size remains nearly unchanged.

As in the case of the cloud point curves,¹ dynamic light scattering results for these microemulsions are essentially independent of the ethane/propane ratio of the continuous phase but found to depend strongly on continuous-phase density. This behavior may be attributed to the near-ideal mixing behavior of ethane and propane at high pressure, their small size, and the absence of steric effects relative to the alkane tails of the surfactant. Over the somewhat narrow concentration range available for this study, we have found that the trends for the diffusion coefficient are consistent with (a) a decrease in droplet-droplet attraction as the distance from the phase boundary increases and (b) an increase in the virial expansion terms which reflect the influence of hydrodynamic and thermodynamic interactions in the generalized Stokes-Einstein equation.

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Surfactant Aggregation Number and Polydispersity of SDS + 1-Pentanol Mixed Micelles in Brine Determined by Time-Resolved Fluorescence Quenching

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Size and polydispersity of sodium dodecyl sulfate (SDS) + 1-pentanol direct mixed micelles have been investigated by means of the time-resolved fluorescence quenching method in the system SDS/1-pentanol/water/NaCl ([SDS] = 0.0331 M, [1-pentanol] = 0.42 M, and [NaCl] = 6.5 g/L of water). This method reveals high polydispersity in micellar size. Several size distribution models have been tested. The one that best fits the data is a double Gaussian distribution which suggests that two populations of mixed micelles might be present in the solution, centered on the SDS mean aggregation numbers of 75 and 830.

Introduction

The time-resolved fluorescence quenching (TRFQ) method has been widely used for the determination of the surfactant aggregation number and of the size of the micelles in direct micellar solution and in oil in water and water in oil microemulsions.¹⁻³ In this method, fluorescent probe and quencher molecules are dissolved in the micelles and, from the analysis of the fluorescence decay curve of the probe, the surfactant aggregation number, N, can be obtained. One reason of the success of this method is that the determination of N is, in principle, independent of intermicellar interactions and micellar shape. Thus, N can be obtained at any surfactant concentration provided that the micelles are not too large or not too small. This is a great advantage over scattering methods where N can be usually accurately obtained only at low micelle concentrations where intermicellar interactions are weak.

In the pioneer⁴⁻⁷ and in the following^{3,8-23} theoretical and experimental works on the TRFQ method it was assumed that

(1) Zana, R. In Surfactant Solutions: New Methods of Investigation: Zana, R., Ed.; Dekker: New-York 1987; Chapter 5, p 241. See references therein.

(2) Grieser, F.; Drummond, C. J. J. Phys. Chem. 1988, 92, 5580. See references therein.

- (3) See: Surfactants in Solution; Mittal, K. L., Lindman, B., Eds.; Plenum Press: New York, 1984.
- (4) (a) Infelta, P. P.; Grätzel, M.; Thomas, J. K. J. Phys. Chem. 1974, 78, 190. (b) Maestri, M.; Infelta, P. P.; Grätzel, M. J. Chem. Phys. 1978, 69, 1522
- (5) Infelta, P. P.; Grätzel, M. J. Chem. Phys. 1979, 70, 179.
- (6) Tachiya, M. Chem. Phys. Lett. 1975, 33, 289; J. Chem. Phys. 1983, 78, 5282; J. Chem. Phys. 1982, 76, 340.
 (7) Atik, S. S.; Singer, L. A. Chem. Phys. Lett. 1978, 59, 519; Ibid 1979,
- 66, 234.
- (8) Atik, S. S.; Nam, M.; Singer, L. A. Chem. Phys. Lett. 1979, 67, 75. (9) Infelta, P. P.; Grätzel, M. J. Chem. Phys. 1983, 78, 5280.
- Yekta, A.; Aikawa, M.; Turro, N. J. Chem. Phys. Lett. 1979, 63, 543.
 Grieser, F.; Tausch-Treml, R. J. Am. Chem. Soc. 1980, 102, 7258.
- (12) Miller, D. J.; Klein, U. K. A.; Hauser, M. Ber. Bunsen-Ges. Phys.
- Chem. 1980, 84, 1135. (13) Dederen, J. C.; Van der Auweraer, M.; De Schryver, F. C. Chem. Phys. Lett. 1979, 68, 451; J. Phys. Chem. 1981, 85, 1198.

micelles are monodisperse in size although, in practice, this is never the case. Thus only a mean micellar aggregation number, $\langle N \rangle$, was determined. However, in the case where the micelles polydispersity is small, $\langle N \rangle$ leads to a good and helpful geometrical representation of the micellar assembly. In fact, it has been shown^{24a} that it may be assumed that a number-average aggregation number is obtained when the polydispersity is low as for small globular micelles. Notice also that N should be then independent of the quencher concentration as indeed found, for instance, for sodium dodecyl sulfate (SDS)19 and cetyltrimethylammonium chloride²⁵ micelles.

More recently, theoretical works have been done that take into account the polydispersity in size of the micelles.^{24,26-28} It has

- (19) Boens, N.; Luo, H.; Van der Auweraer, M.; Reekmans, S.; De Schryver, F. C.; Malliaris, A. Chem. Phys. Lett. 1988, 146, 337.
- (20) Almgren, M.; Swarup, S. (a) J. Colloid Interface Sci. 1983, 91, 256; (b) J. Phys. Chem. 1982, 86, 4212; (c) J. Phys. Chem. 1983, 87, 876.
 (21) Almgren, M.; Löfroth, J.-E.; Van Stam, J. J. Phys. Chem. 1986, 90,
- 4431
 - (22) Fletcher, P. D. I. J. Chem. Soc., Faraday Trans. 1 1987, 83, 1493.
- (22) Fletcher, F. D. I. J. Chem. Soc., Faraday Trans. 1 1987, 83, 1495.
 (23) Lang, J.; Jada, A.; Malliaris, A. J. Phys. Chem. 1988, 92, 1946.
 (24) (a) Almgren, M.; Löfroth, J.-E. J. Chem. Phys. 1982, 76, 2734. (b) Löfroth, J.-E.; Almgren, M. In Surfactants in Solutions; Mittal, K. L., Lindman, B., Eds.; Plenum Press: New York, 1984; Vol. 1, p 627.
 (25) Roelants, E.; Geladé, E.; Van der Auweraer, M.; Croonen, Y.; De Schryver, F. C. J. Colloid Interface Sci. 1983, 96, 288.
 (26) Worr, G. & Griener, F. J. Chem. Soc. Faraday Trans. 1 1996, 82
- (26) Warr, G. G.; Grieser, F. J. Chem. Soc., Faraday Trans. 1 1986, 82, 1813.
- (27) Chen, J.-M.; Su, T.-M.; Mou, C. Y. J. Phys. Chem. 1986, 90, 2418. (28) Almgren, M.; Alsins, J.; Mukhtar, E.; Van Stam, J. J. Phys. Chem. 1988, 92, 4479.

^{(14) (}a) Almgren, M.; Löfroth, J.-E. J. Colloid Interface Sci. 1981, 81,
486. (b) Löfroth, J.-E.; Almgren, M. J. Phys. Chem. 1982, 86, 1636.
(15) Fletcher, P. D. I.; Robinson, B. H. Ber. Bunsen-Ges. Phys. Chem.

^{1981, 85, 863.}

⁽¹⁶⁾ Atik, S. S.; Thomas, J. K. J. Am. Chem. Soc. 1981, 103, 3543.
(17) Lianos, P.; Lang, J.; Zana, R. J. Phys. Chem. 1982, 86, 4809.
(18) Croonen, Y.; Geladé, E.; Van der Zegel, M.; Van der Auweraer, M.;

Vandendriessche, H.; De Schryver, F. C.; Almgren, M. J. Phys. Chem. 1983, 87, 1426 and references therein.

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been shown that for polydisperse micelles the measured value of N (designated by $\langle N \rangle_0$ and called quenching-average aggregation number^{24a}) is dependent on the quencher concentration [Q]. The theory predicts a decrease of $\langle N \rangle_Q$ with increasing [Q].^{24,26} Such a decrease has indeed been observed in several systems.^{24,28-31} We present here the results of a study of the effect of [Q] on the value of N measured by TRFQ in the system made of SDS (0.0331 M), 1-pentanol (0.42 M), and water containing sodium chloride ([NaCl] = 6.5 g/L of water, i.e., 0.1112 M). In this system the micelles are direct mixed micelles of SDS and 1-pentanol. A large decrease of $\langle N \rangle_0$ as [Q] increases has been found. In order to try to explain this variation, several classical micellar size distribution models have been used which, as it will be shown, all failed to account for the data. However, it will be seen that a double micellar distribution accounts very well for the observed variation of $\langle N \rangle_0$ with [Q]. This result leads to the conclusion that two types of mixed micelles might be present in the solution.

Materials and Methods

Materials. SDS was purchased from Touzart et Matignon and twice crystallized in a mixture of water + ethanol. 1-Pentanol was from Merck, and NaCl was from Prolabo (both pro analysis). Cetylpyridinium chloride (CPC), used as quencher, was obtained by reacting pyridine with 1-chlorohexadecane in dry ethanol for 4 h at 135 °C in an autoclave and purified by two crystallizations in ethyl acetate and two crystallizations in acetone. The fluorescent probe, pyrene from Aldrich (99%), was purified by extensive zone refining. We made all solutions by weighing: SDS = 0.963wt %, 1-pentanol = 3.73 wt %, and brine = 95.307 wt %. They were prepared with deionized and distilled water and thoroughly deoxygenated prior to each fluorescence measurement by at least four freeze-pump-thaw cycles. All the fluorescence measurements were made at 18 °C.

Methods. The fluorescence decay curves of micellar solubilized pyrene + CPC (or pyrene alone) were obtained by the single photon counting technique³² and analyzed according to a nonlinear weighted least-squares procedure. It is worth noting that the decay curves were recorded during very long periods of time, sometimes more than 10 h, especially for the systems with low η values. Also, the temperature of the photomultiplier was kept around 10-15 °C. In this manner the analysis of the decay curve could cover a decay of about 2.7 μ s, i.e., about $7\tau_0$, where τ_0 is the fluorescence lifetime of the probe. The determination of N was undertaken either by quenching of pyrene with CPC or, in some cases, by pyrene excimer formation. The N values found with the two types of experiments are in very good agreement (see Figure 1). The excitation wavelength was 335 nm, and the emission was monitored at 380 nm with an interference filter.

All least-squares fittings and other calculations were made with a Victor microcomputer.

Theoretical Section

We shall briefly recall the main equations used for the analysis of our data.

Recall first that for monodisperse micelles the fluorescence decay curves have been shown to obey the equation^{4,6}

$$I(t) = I(0) \exp\{-A_2 t - A_3 [1 - \exp(-A_4 t)]\}$$
(1)

where I(t) and I(0) are the fluorescence intensities at time t and t = 0, respectively, following excitation. A_2 , A_3 , and A_4 are time-independent parameters that can be obtained, together with I(0), by fitting eq 1 to the data.

In the case where the probe and quencher (referred to as reactants in the following) distributions are frozen on the fluorescence time scale (no detectable intermicellar exchange of reactants), the expressions for A_2 , A_3 , and A_4 are⁸

$$A_2 = k_0; \quad A_3 = [Q]/[M]; \quad A_4 = k_q$$
(2)

where $k_0 = 1/\tau_0$ is the fluorescence decay rate constant of the probe in the micelles without quencher and at low pyrene concentration (no excimer formation), [M] is the micelle concentration, and k_a is the pseudo-first-order rate constant for intramicellar quenching of the fluorescence of the probe. In this case the surfactant aggregation number, N (or the number-average surfactant aggregation number in case of small polydispersity), is directly given by

$$N = \frac{C - cmc}{[M]} = \frac{(C - cmc)A_3}{[Q]}$$
(3)

where C is the total surfactant concentration and cmc is the critical micelle (or free surfactant) concentration. The assumptions underlying eqs 1 and 2 are well-known. They have been recalled in several places^{1,14a,24} and will not be given again here.

For the case of polydisperse micelles Almgren and Löfroth^{24a} have proposed a treatment in which the fluorescence decay curve is the sum of all the contributions of the individual micelles. Each micelle contains s surfactant molecules, x quencher, and zfluorescence probes. These authors assume the following: (i) The Poisson distribution of the probes and quenchers among micelles remains valid for each subset of micelles of a particular size (as in the case of monodisperse micelles), but the mean number of probes and quenchers in a micelle is proportional to the aggregation number s, i.e., to the size of the micelle. (ii) The number of probes in a micelle is independent of the presence of a quencher and vice versa. (iii) The intramicellar quenching rate constant (the analogue of k_q in eqs 1 and 2) is proportional to the number of quenchers in the micelles, inversely proportional to the micellar size, and independent of z. Thus, contrary to the monodisperse case where only one value of k_q is considered, in the polydisperse case various values of k_q are considered due to the micellar polydispersity. (iv) The probe and quencher distributions are frozen during the lifetime of the probe. This last assumption is a very severe one since it says that the treatment of Almgren and Löfroth applies only for polydisperse systems where there is no intermicellar exchange of the probe and quencher molecules during the lifetime of the probe. For monodisperse systems, it is well-known^{11,13,16} that when intermicellar exchange of the probe and quencher molecules occurs during the lifetime of the probe, A_2 becomes larger than k_0 . On the other hand, in polydisperse systems even when exchange processes do not occur, a value of A_2 larger than k_0 can be found from fitting eq 1 to the data, if the decay curve is not monitored at sufficient long decay time. Indeed in the polydisperse systems very low values of k_q can exist associated to the largest micelles and the intramicellar quenching can spread over a very long decay time. Therefore, it might be difficult to distinguish between monodisperse systems with exchange of probe and quencher and polydisperse systems with and without ex-change.^{24,32,33} In fact, Almgren and Löfroth showed that a generalization of their treatment to the case of polydisperse systems with exchange of reactants was possible,²⁴ but they emphasized that then it would be difficult to analyze the decay curve and to decide if the observed change of A_2 with [Q] is due to exchange of reactants between micelles or to an appreciable fraction of big micelles with small k_q . This ambiguity did not appear with our system. Indeed, within the accuracy in the determination of A_2 and $k_0, \pm 4\%$, we have found $A_2 = k_0$ for each micellar solution investigated. k_0 has been obtained from the fluorescence decay curve of pyrene by using a relatively low pyrene concentration (molar concentration ratio [pyrene]/[M] < 0.06), avoiding excimer formation, and without CPC in the solution.

The above assumptions lead to the following representation of the decay of the fluorescence in a polydisperse system after pulse excitation at time t = 0:²⁴

^{(29) (}a) Warr, G. G.; Grieser, F.; Evans, D. F. J. Chem. Soc., Faraday Trans. 1 1986, 82, 1829.
(b) Warr, G. G.; Drummond, C. J.; Grieser, F.; Ninham, B. W.; Evans, D. F. J. Phys. Chem. 1986, 90, 4581.
(30) Almgren, M.; Alsins, J.; Van Stam, J.; Mukhtar, E. Prog. Colloid Polym. Sci. 1988, 76, 68.

⁽³¹⁾ Warr, G. G.; Magid, L. J.; Caponetti, E.; Martin, C. A. Langmuir 1988, 4, 813

⁽³²⁾ Malliaris, A.; Lang, J.; Zana, R. J. Phys. Chem. 1986, 90, 655.

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$$I(t) = I(0) \exp(-k_0 t) \frac{\sum_{s} sA(s) \exp[-s\eta[1 - \exp(-K_q t/s)]]}{\sum_{s} sA(s)}$$
(4)

where A(s) represents the concentration of micelles with s surfactant molecules, K_q is the intramicellar quenching rate constant, and η is given by

$$\eta = [Q] / (C - \text{cmc}) \tag{5}$$

which assumes that all the quencher molecules are inside the micelles. This is the case for the CPC quencher used in the present study.

The apparent quenching-average aggregation number is defined as $^{\rm 24a}$

$$\langle N \rangle_{\mathsf{Q}} = \frac{1}{\eta} \ln \left[\frac{I(0)}{I_{\infty}(0)} \right] \tag{6}$$

which is a relation identical with eq 3 where A_3 is obtained with eq 1 from the quantity $\ln [I(0)/I_{\infty}(0)]$. $I_{\infty}(0)$ is the extrapolation at time t = 0 of the decay curve at long time (with slope $A_2 = k_0$).

From eqs 4 and 6 and with assumption (i) (Poisson distribution of the quencher among each set of micelles), $\langle N \rangle_Q$ is finally given by^{24a}

$$\langle N \rangle_{Q} = \frac{1}{\eta} \frac{\sum_{s} sA(s)}{\sum_{s} s \exp(-\eta s)A(s)}$$
 (7)

Notice that at low quencher concentration $(\eta \rightarrow 0)$, $\langle N \rangle_Q$ turns out to be the weight-average aggregation number $\langle N \rangle_W$. In fact, a more general relationship between $\langle N \rangle_Q$ and η , up to order 3 in η , has also been given for dissymmetrical distributions:^{26,34}

$$\langle N \rangle_{\mathbf{Q}} = \langle N \rangle_{\mathbf{W}} - \frac{\sigma^2 \eta}{2} + \frac{\Lambda \eta^2}{6} - \frac{E \eta^3}{24} \tag{8}$$

where σ , Λ , and E are the second, third, and fourth cumulants of the weight distribution sA(s). σ is the root-mean-square deviation, and Λ and E are called the raw skewness and raw excess or kurtosis, respectively. σ^2 and E must be positive, and Λ can take either sign. The skewness and kurtosis are best standardized with respect to a Gaussian (symmetrical) distribution²⁶

$$\lambda = \frac{\Lambda}{2\sigma^3}; \quad \epsilon = \frac{1}{8} \left[\frac{E}{\sigma^4} - 3 \right]$$
(9)

A positive value of λ indicates positive skewness, and positive ϵ indicates that the weight distribution sA(s) is more peaked about $\langle N \rangle_{\mathbf{W}}$ than in a Gaussian distribution.

An additional remark must be made that concerns the use, in few cases, of pyrene excimer formation for the determination of $\langle N \rangle_Q$ in our study, while the theory of Almgren and Löfroth is made for the case where fluorescent probe and quencher are used. As already mentioned, no significant differences were found in the $\langle N \rangle_Q$ values obtained with pyrene excimer and pyrene-CPC. Therefore, if the theory of Almgren and Löfroth applies to our system, it seems also to be valid when excimer formation is employed.

Results and Discussion

As pointed out by Almgren and Löfroth,^{24a} $\langle N \rangle_Q$ can be obtained by fitting eq 1 to the data, which gives A_3 or, which is equivalent, $\ln [I(0)/I_{\infty}(0)]$. The fits of eq 1 to our fluorescence decay curves were very good, as good as those that we obtain usually for monodisperse micelle of relatively moderate surfactant aggregation number, around 100. Knowing A_3 , $\langle N \rangle_Q$ is then calculated with eq 3 or 6. The values of $\langle N \rangle_Q$ determined by using this procedure are shown in Figure 1 as a function of η . In eqs



Figure 1. Variation of the SDS quenching-average aggregation number $\langle N \rangle_{\rm Q}$ versus η , determined with CPC as quencher (\bullet) and with pyrene excimer formation (O). The vertical bars are the estimated experimental uncertainty in the determination of $\langle N \rangle_{\rm Q}$. The full line is the best fit of eq 8 to the data. It has been obtained with $\langle N \rangle_{\rm W} = 513$, $\sigma = 328$, $\Lambda = 1.47 \times 10^7$, and $E = 8.78 \times 10^8$.

3 and 5 [Q] has been replaced by [P], the pyrene concentration, when pyrene excimer was used and the cmc has been taken equal to 7.5×10^{-4} M. This value has been estimated from the decrease of the cmc of SDS upon addition of 1-pentanol^{35,36} and NaCl^{37,38} to SDS micellar solutions. Note that in Figure 1 η and therefore [Q] has been varied by a factor 60.

At this point it must be recalled that Almgren et al.²⁸ have shown, for a hypothetical but realistic polydisperse case, that the $\langle N \rangle_0$ values determined with eq 1 are considerably underestimated. This result was obtained by using simulated decay curves generated for a given dissymmetrical micellar size distribution and a given variation law of the intramicellar quenching rate constant versus micellar size. In spite of the fact that this result has been obtained for a particular polydisperse case and with simulated decay curves that were much less extended than in the present study (1.5 μ s compared to 2.7 μ s with identical probe lifetime), it might well be that our $\langle N \rangle_0$ values are underestimated. However, this would not modify the main conclusion given in the following, which is that the investigated system seems to contain two types of mixed micelles. This conclusion is even strengthened if one assumes that the $\langle N \rangle_{Q}$ values are more underestimated for the lowest than for the largest η values, as inferred by Almgren et al.²⁸ from their simulation analysis. Therefore, considering the fact that the fits of eq 1 to our fluorescence decay data were very good, as said previously, and that there is at the present time no unquestionable method for the determination of $\langle N \rangle_0$, only eq 1 has been used in the present study.

The continuous curve in Figure 1 represents the best fit of eq 8 to the data, obtained with $\langle N \rangle_W = 513$, $\sigma^2 = 1.077 \times 10^5$ ($\sigma = 328$), $\Lambda = 1.47 \times 10^7$, and $E = 8.78 \times 10^8$. As expected, σ^2 and E are positive. $\lambda = 0.208$ reflects a positive skewness, and $\epsilon = -0.366$ seems to indicate that the weight distribution sA(s) is less peaked about $\langle N \rangle_W$ than in a Gaussian distribution. Note that the fitted curve is close to the experimental points but presents, however, a small minimum around $\eta = 0.019$ and a small inflection around $\eta = 0.022$. Notice that if the data point at $\eta = 0.031$ (last data point to the right) is not considered, no minimum appears in the curve that best fits the data. The adjusted parameters are then $\langle N \rangle_W = 547$, $\sigma = 368$, $\Lambda = 2.27 \times 10^7$, and $E = 1.71 \times 10^9$ ($\lambda = 0.2277$, $\epsilon = -0.363$). Again λ is positive which indicates a positively skewed micellar size distribution.

In order to try to obtain more information about the type of micelle size distribution in our system, we have tested the following model distribution functions A(s):

(i) Gaussian:^{24,26}

$$A(s) = A(s_{\rm N}) \exp[-(s - s_{\rm N})^2 / 2\sigma^2]$$
(10)

- (37) Newbery, J. E. Colloid Polym. Sci. 1979, 257, 773.
- (38) Binana-Limbele, W.; Zana, R. Colloids Surf. 1986, 21, 483.

⁽³⁴⁾ Brown, W.; Rymdén, R.; Van Stam, J.; Almgren, M.; Svensk, G. J. Phys. Chem. 1989, 93, 2512.

⁽³⁵⁾ Hayase, K.; Hayano, S. J. Colloid Interface Sci. 1978, 63, 446; Bull. Chem. Soc. Jpn. 1977, 50, 83.

⁽³⁶⁾ Jain, A. K.; Singh, R. P. B. J. Colloid Interface Sci. 1981, 81, 536.



Figure 2. Best fit of the theoretical variation of $\langle N \rangle_Q$ versus η to the data with a Gaussian distribution function (eq 13). Curve 1 represents the best fit with all the data and curve 2 that with the data at η below 0.006. The values of the fitting parameters are $\langle N \rangle_W = 310$ and $\sigma = 127$ for curve 1 and $\langle N \rangle_W = 540$ and $\sigma = 320$ for curve 2.

where $s_N = \langle N \rangle_N$ is the number-average aggregation number and σ is the root-mean-square deviation of s.

(ii) exponential:24,26

$$A(s) = A(s_0) \exp[-(s - s_0) / \sigma] \qquad s \ge s_0$$

$$A(s) = 0 \qquad s < s_0 \qquad (11)$$

where s_0 is the starting value of s for the distribution and σ is a measure of the decay length of the distribution. (iii) zero-order logarithmic normal distribution (ZOLD):³⁹

$$A(s) = \frac{\exp[-(\ln s - \ln s_{\rm M})^2 / (2\sigma_0^2)]}{(2\pi)^{1/2} \sigma_0 s_{\rm M} \exp(\sigma_0^2 / 2)}$$
(12)

where $s_{\rm M}$ is the modal value of s (i.e., s value at the maximum of the distribution) and σ_0 is a parameter that is a measure of the width and skewness of the distribution. The advantage of this distribution is that one can explore the effect of the width of the distribution while the modal value stays fixed.³⁹

Almgren and Löfroth²⁴ have given the analytical expression of $\langle N \rangle_Q$ as a function of η for Gaussian and exponential distributions. They are

(i) for the Gaussian distribution:

$$\langle N \rangle_{\rm Q} = \langle N \rangle_{\rm N} + \sigma^2 \left[\frac{1}{\langle N \rangle_{\rm N}} - \frac{\eta}{2} \right] = \langle N \rangle_{\rm W} - (\sigma^2/2)\eta \qquad (13)$$

(ii) for the exponential distribution:

$$\langle N \rangle_{\rm Q} = s_0 + \frac{2}{\eta} \ln (1 + \eta \sigma) - \frac{1}{\eta} \ln \left[1 + \frac{\eta s_0 \sigma}{s_0 + \sigma} \right]$$
(14)

Curve 1 in Figure 2 shows the best fit of eq 13 to the data, obtained with $\langle N \rangle_W = 310$ and $\sigma = 127$. With these values $\langle N \rangle_N$ is found equal to 244. Obviously the fit is not good at all, and this was expected because the Gaussian distribution is a symmetrical distribution which leads theoretically to a linear variation of $\langle N \rangle_Q$ versus η , whereas a large curvature has been found experimentally. Curve 2 in Figure 2 shows the best fit of eq 13 to the data determined for the domain of η below 0.006. This fit has been obtained with $\langle N \rangle_W = 540$ and $\sigma = 319$. In this low η concentration range, eq 13 fits well the data. However, in this case $\sigma > \langle N \rangle_W/2$, and it is therefore not possible to calculate a value for $\langle N \rangle_N$. This indicates that, with the data obtained for η below 0.006, the distribution cannot be Gaussian either. A similar result was found with a oil in water microemulsion based on SDS.²⁴

In the case of the exponential distribution it was not possible to obtain directly the best fit of eq 14 to the data with the two adjustable parameters s_0 and σ . Therefore, fixed values for s_0 were

TABLE I: Values of σ That Give the Best Fit of Eq 14 (Exponential Distribution) to the Data, for Several Fixed Values of s_0^a

<i>s</i> 0	σ	10 ⁻³ ∑Δ ²	$\langle N \rangle_{\mathbf{W}}$					
2	197	145	394					
100	127	339	297					
180	3	769	183					

^a The corresponding curves are shown in Figure 3. $\sum \Delta^2$ is the sum of the deviations squared, and $\langle N \rangle_W$ is the weight-average aggregation number.

TABLE II: Values of σ_0 That Give the Best Fit of Eqs 7 and 12 (ZOLD) to the Data, for Several Fixed Values of s_M^a

s _M	σ_0	$10^{-3}\Sigma\Delta^2$	$\langle N \rangle_{\mathbf{W}}$	
10	1.38	25.2	691	
50	0.98	74.7	513	
100	0.75	164	397	
200	0.38	367	286	

^a The corresponding curves are shown in Figure 4. $\sum \Delta^2$ is the sum of the deviations squared, and $\langle N \rangle_{\mathbf{W}}$ is the weight-average aggregation number.



Figure 3. Best fit of the theoretical variation of $\langle N \rangle_Q$ versus η to the data with an exponential distribution function (eq 14) for three fixed values of the parameter s_0 (see text). The values of the fitting parameter σ and of $\sum \Delta^2$ and $\langle N \rangle_W$ are given in Table I.

chosen and the best fit of eq 14 to the data was determined with σ as adjustable parameter. Table I gives the values obtained for σ with three different values of s_0 . Table I gives also the corresponding sum of deviations squared, $\sum \Delta^2$, and $\langle N \rangle_{\rm W}$ calculated from eq 14 as $\eta \rightarrow 0$. The $\sum \Delta^2$ values indicate that the best fit is obtained with $s_0 = 2$, which is physically not reasonable. Moreover, as it is seen in Figure 3 where the curves relative to the values of s_0 and σ given in Table I are shown, the fits are very poor especially for $s_0 > 2$.

No analytical relationship for the variation of $\langle N \rangle_0$ versus η has been given in case of the ZOLD. We have therefore generated the variation of $\langle N \rangle_0$ as a function of η using eqs 7 and 12 and determined, with a nonlinear weighted least-squares method, the parameters $s_{\rm M}$ and σ_0 that give the best fit of eq 7 to the data. As in the case of the exponential distribution, no fit could be found with two adjustable parameters, namely here $s_{\rm M}$ and σ_0 . Therefore the fits were performed with various fixed values of s_{M} and with σ_0 as adjustable parameter. It was not necessary to use the step $\Delta s = 1$ in the sums appearing in eq 7. We have checked in many examples that the same values of $s_{\rm M}$ and σ_0 were found with Δs = 5, which saved computer time. In these sums the largest value used for s was the one for which the ratio $A(s)/A(s_M)$ became lower than 10⁻⁴. Table II shows the values of σ_0 that give the best fit of eq 7 to the data, for various values of s_M , together with the values of $\sum \Delta^2$ and $\langle N \rangle_W$ calculated for each distribution with the relationship $\langle N \rangle_{\rm W} = \sum s^2 A(s) / \sum s A(s)$. Table II and Figure 4 show that the quality of the fit increases as s_{M} decreases. In fact, even better fits (lower values of $\sum \Delta^2$) have been found for $s_{\rm M}$ below 10, up to 2.

Since relatively good fits has been obtained for $s_M < 10$, one can wonder if the ZOLD is not a good micelle size distribution model for our system. Figure 5 visualizes the ZOLD micellar distribution with two couples of values of s_M and σ_0 taken from

⁽³⁹⁾ Espenscheid, W. F.; Kerker, M.; Matijević, E. J. Phys. Chem. 1964, 68, 3093.

TABLE III: Values of P, s_{N1} , σ_1 , s_{N2} , and σ_2 That Give Good Fits of Eqs 7 and 16 (Two-Gaussian Distribution) to the Data (Fits a-d) and Values of P, s_{N1} , and s_{N2} That Give the Best Fit of Eq 7 to the Data with Two Monodisperse Micelle Populations (Fit e)^a

				-			•	• •			
 fit	figure	curve	Р	<i>s</i> _{N1}	σ_1	s _{N2}	σ2	$10^{-3}\Sigma\Delta^2$	W%	$\langle N \rangle_{W}$	
a	6	1	80	90	20	914	243	14.2	39.3	631	
b	6	2	5	60	10	750	9	10.5	29.4	548	
с			3	75	20	840	10	9.6	34.7	572	
d			0.5	80	40	920	3	11	39.3	597	
e	7		5.62	75		828		9.5	33.7	574	

 $a \sum \Delta^2$ is the sum of the deviations squared, W% is the weight percent of the surfactant in the lowest micellar size distribution, and $\langle N \rangle_{W}$ is the weight-average aggregation number.



Figure 4. Best fit of eq 7 to the data with ZOLD function (eq 12), for four fixed values of the parameter s_M (see text). The value of the fitting parameter σ_0 and of $\sum \Delta^2$ and $\langle N \rangle_W$ are given in Table II.



Figure 5. Variation of A(s) versus s for the ZOLD function with $s_M = 10$ and $\sigma_0 = 1.38$ (curve 1) and with $s_M = 50$ and $\sigma_0 = 0.98$ (curve 2). The distribution functions have been normalized to the maximum at A(s) = 1. These curves illustrate two of the micellar size distributions used in the fits of eq 7 to the data with the ZOLD function (eq 12) (see Figure 4 and Table II).

Table II, namely, $s_M = 10$ and $\sigma_0 = 1.38$ (curve 1) and $s_M = 50$ and $\sigma_0 = 0.98$ (curve 2). These curves show that the distribution expands to large aggregation numbers, but the low values found for s_M , especially for curve 1 which gives a better fit than curve 2 to the variation of $\langle N \rangle_Q$ versus [Q], are questionable.

Low values of the mean aggregation number of SDS in aqueous solutions of 1-pentanol have been found in other studies. For instance, $N = 20^{40}$ and 26.9^{20a} have been measured in aqueous solution with 0.1 M SDS + 0.4 M 1-pentanol and with 0.0331 M SDS + 0.227 M 1-pentanol, respectively. Values of N close to 20 have also been found with 0.25 M SDS + 0.4 M 1-pentanol.^{14a} Thus, as far as the effect of 1-pentanol on the aggregation number of SDS is concerned, it is not physically unlikely that aggregates containing a small number of SDS ions are present in the system. However, the addition of 0.1 M NaCl to solutions of SDS in pure water and to aqueous solutions of 0.2 M SDS + 0.6 M 1-pentanol has been found to increase N from about 65 to 93^{14a,18} and from 47 to 197,⁴⁰ respectively. Thus a larger increase of N is observed in SDS + 1-pentanol mixed micelles upon addition of 0.1 M NaCl compared to its increase in SDS solution without 1-pentanol. It seems therefore that an aggregation number larger than 20 should be found for the maximum in the

(40) Lianos, P.; Lang, J.; Strazielle, C.; Zana, R. J. Phys. Chem. 1982, 86, 1019.



Figure 6. Best fits of eq 7 to the data with the sum of two Gaussian distributions (eq 16). The corresponding parameters P, s_{N1} , σ_1 , s_{N2} , and σ_2 are obtained as described in the text, and their values are given in Table III.

micelle size distribution, but it seems difficult, at the present time, to definitively rule out the ZOLD as a distribution model for our system. We will see now that another micellar distribution model, however, accounts perfectly well for our results.

The last model that has been tested is the sum of two Gaussian distributions

$$A(s) = A(s_{N1}) \exp\left[\frac{-(s - s_{N1})^2}{2\sigma_1^2}\right] + A(s_{N2}) \exp\left[\frac{-(s - s_{N2})^2}{2\sigma_2^2}\right] (15)$$

where s_{N1} and s_{N2} are the value of s at the maximum of the two distributions and σ_1 and σ_2 are the root-mean-square deviations of s for the two distributions. Equation 15 also may be written as

$$A(s) = A(s_{N2}) \left[P \exp\left[\frac{-(s - s_{N1})^2}{2\sigma_1^2}\right] + \exp\left[\frac{-(s - s_{N2})^2}{2\sigma_2^2}\right] \right]$$
(16)

where $P = A(s_{N1})/A(s_{N2})$. Once eq 16 has been introduced in eq 7, $A(s_{N2})$ is eliminated and only five parameters are needed to describe the double Gaussian distribution: $P, s_{N1}, \sigma_1, s_{N2}$, and σ_2 . It was not possible to fit eq 7 to the data with these five quantities as adjustable parameters in our least-squares fitting procedure. We also failed in our attempts to fit eq 7 to the data with only four or three adjustable parameters. We have finally employed the following method. Fixed values have been chosen for P, s_{N1} , and σ_1 , and eq 7 has been fitted to the data with s_{N2} and σ_2 as adjustable parameters. The various values tested for P, s_{N1} , and σ_1 were between 0.06 and 150, 50 and 120, and 1 and 60, respectively. Values outside these ranges were expected to give very poor fits of eq 7 to the data. In the sums in eq 7 the lowest and highest s values were calculated so that the amplitude A(s) was below 1/200 of the maximum amplitude in each Gaussian distribution, and the step for s, Δs , was a function of the width of the Gaussian distributions. At least 10 values of swere used for the narrowest distribution. We have checked, in several examples, that the same values were found for the adjustable parameters, if a greater number of s values was used. In each of the two Gaussian distributions (eq 15) Δs was, of course, identical.



Figure 7. Best fit of eq 7 to the data with two monodisperse micelle populations. This fit has been obtained with P = 5.62, $s_{N1} = 75$, and s_{N2} = 828 (see text and Table III).

Figure 6 shows two curves that fit well the experimental data. The corresponding values of the parameters are given in Table III (fits a and b). Fits c and d (see Table III) give values of $\sum \Delta^2$ lower than those for fit a, and the corresponding curves (not shown in Figure 6) are even closer to the data points than curve 1. The values in Table III indicate that good fits can be obtained with different values of P, s_{N1} , σ_1 , s_{N2} , and σ_2 . In particular, very different values of P, σ_1 , and σ_2 are found that give good fits of eq 7 to the data. Note that large differences in the value of σ_2 are found, between 3 and 240, so that the method leads to a very unprecise determination of σ_2 . The determination of σ_1 , although not very good, is better, between 10 and 40. On the other hand, the values of s_{N1} and s_{N2} seems fairly well determined. They are around 75 \pm 20 and 830 \pm 100, respectively.

We have also considered the case of two sets of monodisperse micelles, of micellar aggregation number s_{N1} and s_{N2} , as model distribution to account for our data. In this case eq 16 reduces to A(s) = P + 1, and eq 7 could be fitted to the data with the three unknowns P, s_{N1} , and s_{N2} as adjustable parameters. Figure 7 shows the best fit of eq 7 to the data. The corresponding values of P, s_{N1} , s_{N2} , and $\sum \Delta^2$ are given in Table III (fit e). These values are in agreement with those found with the two Gaussian distributions and a different fitting procedure. It shows that the best fit is obtained for a value of P close to 5 and that the two types of micelles have an aggregation number around 75 and 830. Comparison of the curves in Figures 3, 4, 6, and 7 and the values of $\sum \Delta^2$ in Tables I-III shows that a much better fit is obtained with the double Gaussian or the two monodisperse micelle distributions than with the ZOLD or the exponential distribution. Some evidence for the existence of two types of micelles in aqueous solutions of SDS + 1-pentanol has been provided from some thermodynamic measurements.⁴¹ These measurements seem to indicate that 1-pentanol + SDS mixed micelles can be formed not only by solubilization of 1-pentanol in SDS micelles but also, at high 1-pentanol/SDS ratio, by cosolubilization of SDS and 1-pentanol in 1-pentanol-rich aggregates. The presence of salt in our system would even enhance this effect, since addition of salt certainly decreases the solubility of 1-pentanol in water. However, other results are necessary to confirm this conclusion. The result given here must only be taken as a clue for the still hypothetical presence of two populations of SDS + 1-pentanol mixed micelles in the investigated system. Moreover, in their treatment Almgren and Löfroth²⁴ have made some assumptions that might no longer be valid with the presence in the solution of two micellar populations having different 1-pentanol/SDS ratios. For instance, they assume that the mean occupancy number of quenchers in the micelles is proportional to the size of the micelles, i.e., to s. If there are large differences in the 1-pentanol/SDS ratios, the size of the micelles is no longer proportional to s and some corrections must then be introduced in the treatment.

The phase behavior of the SDS/1-pentanol/water/NaCl system has been extensively studied in the water-rich region by Guérin

and Bellocq.^{42a} These authors have shown the high complexity of the phase diagram in this region and have carefully examined many aspects of it. They have shown that a birefringent zone appears in this region as the NaCl concentration increases above 6 g/L of water. The system studied here is at a composition close to this birefringent zone which is close to a lamellar phase.⁴² It is of course not clear yet if the structural complexity of the solution is related to the proximity of this birefringent zone and/or of the lamellar phase, and more work has to be done with other techniques and at other compositions and temperatures of the system before this point can be elucidated.

Finally it can be argued that other positively skewed distributions, as for instance the Schulz⁴³ or the Stevenson-Heller-Wallach⁴⁴ distributions, have not been explored in the present work. The skewness of these two distributions is lower than for the ZOLD.⁴⁵ With these distributions the best fits of eq 7 to the data will be between those found with the ZOLD and with the Gaussian distribution and are therefore expected to be rather poor. Also, no negatively skewed distribution^{46,47} has been explored. The reason is that the fit of eq 8 to the data seems to indicate that, in order to account for the observed variation of $\langle N \rangle_0$ versus η , a positively skewed distribution must be used (recall that in the fit of eq 8 to the data Λ , and therefore λ , has been found positive). It must be finally noticed that the value close to 5 found for P for the best fits of the double Gaussian and of the two monodisperse micelle distributions agrees with the positively skewed distribution predicted from the fit of eq 8 to the data.

Conclusion

Using a theory developed by Almgren and Löfroth,^{24a} we have shown that in the system SDS (0.0331 M)/1-pentanol (0.42 M)/water/NaCl (6.5 g/L of water) mixed micelles of SDS + 1-pentanol are highly polydisperse. Several simple distribution functions failed to account satisfactorily for the experimental decrease of the SDS quenching-average aggregation number $\langle N \rangle_0$ as the quencher concentration increases. A distribution function composed of two Gaussian distributions or of two monodisperse micelles gives very good fits of the theoretical variation of $\langle N \rangle_0$ versus η to the data. These fits suggest that two populations of mixed micelles are perhaps present in the solution. These two populations of micelles would have 75 and 830 as mean SDS aggregation number, respectively. An extensive study of the phase diagram of SDS/1-pentanol/water/NaCl made by Guerin and Bellocq,⁴² especially in the water-rich corner, has shown that various phases and critical points are present in the system depending on NaCl concentration and temperature. The system studied here has a composition close to a lamellar phase and to a birefringent zone⁴² which might be the reason for the complexity of the structural composition of the solution. Unfortunately there is, at the present time, no easy and accurate direct determination of two mean micellar aggregation numbers in the same micellar solution, except perhaps the TRFQ method used here. Only a systematic exploration of the structure of the micellar solutions in the water-rich corner of the SDS/1-pentanol/water/NaCl phase diagram might help to give more insight into the real structure of the solutions. More works are now in progress in order to closely compare the TRFQ and other measurements to the results of the phase diagram investigations, at various compositions and temperatures of this quaternary system.

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(46) Wallace, T. P.; Kratohvil, J. P. J. Polym. Sci., Part A2 1972, 10, 631. (47) Rowell, R. L.; Kratohvil, J. P.; Kerker, M. J. Colloid Interface Sci. 1968, 27, 501.

^{(42) (}a) Guérin, G.; Bellocq, A. M. J. Phys. Chem. 1988, 92, 2550. (b)
Guérin, G.; Bellocq, A. M.; Roux, D. Personal communication.
(43) Schulz, G. V. Z. Phys. Chem. 1939, B43, 25.
(44) Stevenson, A. F.; Heller, W.; Wallach, M. L. J. Chem. Phys. 1961, 34, 1789. Heller, W.; Wallach, M. L. J. Phys. Chem. 1963, 67, 2577.
(45) Yan, Y. D.; Clarke, J. H. R. Adv. Colloid Interface Sci. 1989, 29, 277 277

⁽⁴¹⁾ De Lisi, R.; Genova, C.; Testa, R.; Turco Liveri, V. J. J. Solution Chem. 1984, 13, 121.