

Fluorescence Study of the Aggregation Behavior of Different Surfactants in Aqueous Solutions in the Presence and in the Absence of Gas

R. G. Alargova,[†] I. I. Kochijashky,[†] and R. Zana*

Institut C. Sadron (CRM-EAHP), 6, rue Boussingault, 67000 Strasbourg, France

Received September 8, 1997. In Final Form: December 8, 1997

The effect of dissolved gas (air, argon, butane) on the properties of aqueous surfactant micelles (aggregation number, microviscosity and micropolarity) has been investigated by means of time-resolved fluorescence quenching and spectrofluorometry on a large number of surfactant systems differing by the nature of the surfactant (anionic, cationic, zwitterionic, and nonionic) and the temperature. The investigated properties were found to be independent of the state of the system: air-saturated, argon-saturated, or degassed. In the particular case of micellar solutions of cetyltrimethylammonium chloride, where the measurements involved 10 identical solutions, the average aggregation numbers measured for air-saturated, argon-saturated, and degassed solutions differed by less than 1%. The results indicate that if the hydrophobic interaction, which is the driving force for micelle formation, is affected by the dissolved gas, this would be to a very small extent, well below the sensitivity level of the methods of investigation of micellar solutions used in this study.

1. Introduction

Surfactants organize themselves into micelles when solubilized in water at concentrations above the critical micellization concentration (cmc). The micelle size and shape are mainly determined by the characteristics of the surfactant: length l and volume v of the hydrophobic moiety and optimal surface area a of the hydrophilic headgroup which combine into the surfactant packing parameter $P = v/al$.^{1,2} Different factors can influence the number of surfactants making up a micelle. Thus, an increase of temperature can lead in the case of nonionic surfactants to a large increase in the micelle aggregation number.^{3,4} The acidity of the aqueous phase is important for the micellar properties of zwitterionic surfactants.⁵ The addition of electrolyte to micellar solutions of ionic surfactants can bring about large increases in micelle aggregation number, owing to the screening of electrostatic interactions.^{2,6–8} Recall, as this is important for the present study, that gases that are sparingly soluble in water, such as short-chain alkanes, argon, and oxygen, exhibit a markedly larger solubility in the presence of micelles.^{2,9–12}

The driving force for micelle formation in aqueous solutions is the so-called hydrophobic interaction.^{1,2} Despite the widespread use of the “hydrophobic interaction” concept (very few studies dealing with aqueous solutions of compounds with molecules containing apolar groups do not mention the “hydrophobic interaction” or the “hydrophobic effect”), much research is still devoted to characterize this interaction and understand its origin. Recently, it has been reported that the air (gas) solubilized in water may play an important role in various interfacial phenomena: time dependence of the surface tension of water,¹³ emulsion stability, emulsion polymerization, and surfactant aggregation,¹⁴ and forces between hydrophobic polypropylene surfaces.¹⁵ These observations and others^{16–18} suggest that the hydrophobic interaction may be influenced or mediated by the dissolved gas.

In view of the importance of the hydrophobic interaction in a large body of studies dealing with aqueous solutions, any piece of information that will permit a better assessment of the possible effect of solubilized gases is deemed useful. We felt that the techniques available in our laboratory were able to provide such information. Indeed, from the above, one expects the properties of micelles, particularly their aggregation number, to depend on whether gas is present or absent, and eventually to also depend on the nature of the solubilized gas, if gas indeed affects the hydrophobic interaction. Measurements of micelle aggregation numbers are performed in our laboratory on a routine basis by means of the so-called time-resolved fluorescence quenching method (TRFQ).¹⁹ This

* To whom correspondence should be addressed.

[†] On leave of absence from the Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, University of Sofia, Sofia, Bulgaria.

(1) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1991; Chapter 17.

(2) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley: New York, 1980; Chapter 7.

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

(4) Binana-Limbélé, W.; Zana, R. *J. Colloid Interface Sci.* **1988**, 121, 81.

(5) Lomax, E. G. *Amphoteric Surfactants*; M. Dekker: New York, 1996.

(6) Mazer, N. A. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum Press: London, 1991; Chapter 17.

(7) Missel, P. J.; Mazer, N. A.; Carey, M. C.; Benedek, G. B. *J. Phys. Chem.* **1989**, 93, 8354.

(8) Alargova, R.; Petkov, J.; Petsev, D.; Ivanov, I. B.; Broze, G.; Mehreteab, A. *Langmuir* **1995**, 11, 1530.

(9) Rosen, M. J. *Surfactants and Interfacial Phenomena*; John Wiley: New York, 1989.

(10) Ownby, D.; Prapaitrakul, W.; King, A. D., Jr. *J. Colloid Interface Sci.* **1988**, 125, 526 and references therein.

(11) King, A. D., Jr. *J. Colloid Interface Sci.* **1990**, 137, 577

(12) Serra, M. C. C.; Coelho, J. A. P.; Calado, J. C. G.; Palavra, A. M. F. *J. Colloid Interface Sci.* **1995**, 173, 278.

(13) Sobol, H.; Garfias, J.; Keller, J. *J. Phys. Chem.* **1976**, 80, 1941.

(14) Karaman, M. E.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1996**, 100, 15503.

(15) Meagher, L.; Craig, V. S. T. *Langmuir* **1994**, 10, 2736.

(16) Craig, V. S.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1993**, 97, 10192.

(17) Craig, V. S.; Ninham, B. W.; Pashley, R. M. *Nature* **1993**, 364, 317.

(18) Bunkin, N. F.; Kiseleva, O. A.; Lobeyev, A. V.; Movchan, T. G.; Ninham, B. W.; Vinogradova, O. I. *Langmuir* **1997**, 13, 3024.

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

Table 1. Surfactant Used in the Fluorescence Experiments

surfactant type	name	abbreviation	cmc (mM)
anionic	sodium dodecyl sulfate	SDS	8.0 ²¹
	dodecyltrimethylammonium chloride	DTAC	21.5 ²¹
cationic	hexadecyltrimethylammonium chloride	CTAC	1.3 ²¹
	tetradecyltrimethylammonium bromide	TTAB	0.42 ²¹
zwitterionic	benzyltrimethyl- <i>n</i> -hexadecylammonium chloride	BHDC	0.20 ²¹
	dodecyltrimethylammonium propyl sulfonate	C ₁₂ N ₃ SO ₃	3.56 ²²
nonionic	dodecyltrimethylammonium propyl carbonate	C ₁₂ N ₃ CO ₂	4.3 ²²
	hexaethyleneglycol monododecyl ether	C ₁₂ E ₆	0.08 ²¹
	octaethyleneglycol monododecyl ether	C ₁₂ E ₈	0.1 ²⁰
	Triton X100	TX100	0.30 ²³

method uses a fluorescent probe, generally pyrene, and a quencher of the pyrene fluorescence. Both the probe and quencher are fully solubilized in the micelles. The analysis of the fluorescence decay curves in conditions well described in the literature¹⁹ yields the molar concentration ratio $R = [\text{quencher}]/[\text{micelle}]$ and the rate constant for intramicellar quenching, k_q . The aggregation number N is obtained from the value of R according to $N = R([\text{surfactant}] - \text{cmc})/[\text{quencher}]$. The product Nk_q is a measure of the viscosity sensed by the probe and quencher in their motion in the micelles.¹⁹ Molecular oxygen is a strong quencher of the pyrene fluorescence²⁰ and it is customary in our laboratory to *completely* remove the solubilized air by successive freeze–pump–thaw cycles and work on the deaerated solutions or saturate them with argon, prior to the measurements. The values of N and k_q can thus be obtained with *aerated solutions, completely degassed solutions, and solutions that are saturated with any readily available gas.*

We report below the results for two series of systems. The first series concerns 23 surfactant solutions differing by the nature of the surfactant—*anionic, cationic, nonionic and zwitterionic*—and/or the temperature at which the measurements were performed. As these solutions were available, we also performed measurements of the pyrene intensity ratio I_1/I_3 of the first and third peaks in the emission spectrum of pyrene, often referred to as polarity index, as it is sensitive to the polarity sensed by pyrene in its microenvironment.¹⁹ The second series of experiments involved 10 identical solutions of cetyltrimethylammonium chloride which we investigated to set a limit on the possible effect of solubilized gas on the micelle aggregation number. Within the experimental error, the aggregation number, the microviscosity, and the micropolarity were found to be insensitive to the presence or absence of solubilized gas and to its nature.

The paper is organized as follows. The coming section describes the materials and experimental procedures. Section 3 deals with the experimental results. A brief discussion and concluding remarks are given in Section 4.

2. Experimental Section

The surfactants used in this study are listed in Table 1. Their synthesis, purification, and cmc have been reported.^{3,4,21–25} All fluorescence experiments were carried out with pyrene as a fluorescent probe. The quenchers were dodecylpyridinium ion in the case of sodium dodecyl sulfate, tetradecylcyanopyridinium

ion for Triton X100, and cetylpyridinium ion for all other samples.^{24–27} All quenchers were used under the form of their chloride salts.

The fluorescence decay curves were recorded using a single photon counting apparatus.^{19,24–27} The general decay equation:¹⁹

$$I(t) = I(0)\exp\{-A_2t - A_3[1 - \exp(-A_4t)]\} \quad (1)$$

was fitted to the decay curves using a nonlinear weighted least squares procedure.^{24–27} $I(t)$ and $I(0)$ are the fluorescence intensities at time t and zero, following the excitation. A_2 , A_3 and A_4 are three constants which are determined as adjustable parameters. The ratio between the molar concentrations of pyrene, $[P]$, and micelles, $[\text{micelle}]$, was kept below 0.01 to prevent the formation of pyrene excimer. The molar concentration ratio $R = [\text{quencher}]/[\text{micelle}]$ was adjusted as to be close to 1. For most of the investigated systems the constant A_2 was found to be equal to $1/\tau$, reciprocal of the pyrene lifetime determined in a separate experiment, performed in the absence of quencher. In this case, the constants A_3 and A_4 are given by¹⁹

$$A_3 = R = [\text{quencher}]/[\text{micelle}] \quad (2)$$

$$A_4 = k_q \quad (3)$$

where k_q is the pseudo-first-order rate constant for intramicellar quenching.

For each solution, the fluorescence decay curves were recorded (1) with the air-saturated solution (the concentration of solubilized gas is around 2 mM at normal temperature and pressure),¹⁴ (2) after a complete removal of the air by three freeze–pump–thaw cycles,^{19,27} and (3) after saturation of the solution with argon. The fluorescence cell which permits the degassing of the solutions and their regassing has been fully described.²⁷ To avoid systematic deviations in the final results due to the experimental procedure, for some surfactant solutions the decay curve was first recorded with the deaerated solution, second after saturating the solution with argon, and last after saturation with air.

The fluorescence emission spectra of micelle-solubilized pyrene in some of the investigated solutions were recorded by means of a Hitachi F 4010 spectrofluorometer at an excitation wavelength of 335 nm. They were used to obtain the ratio I_1/I_3 of the fluorescence intensities of the first and third vibronic emission peaks.

3. Results and Discussion

Micelle Aggregation Numbers. Table 2 lists the values of the aggregation numbers (N) measured for the different solutions of ionic, nonionic and zwitterionic surfactants investigated, which range between 33 and 181. The surfactant solutions are numbered in the order of increasing N value. For each surfactant, the measurements were carried out at a given surfactant concentration, generally much larger than the cmc, and in several cases at different temperatures. The examination of Table 2

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

(21) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS 36—National Standard Reference Data Systems—NBS 36; NBS: Washington, DC, 1971.

(22) Chevalier, Y.; Stout, Y.; Pourchet, S.; Le Perchec, P. *Langmuir* **1991**, *7*, 848.

(23) Funasaki, N.; Hada, S.; Neya, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1725.

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

(25) Alami, E.; Van Os, N. M.; Rupert, L. A.; De Jonc, B.; Kerkhoh, F. J.; Zana, R. *J. Colloid Interface Sci.* **1993**, *160*, 205.

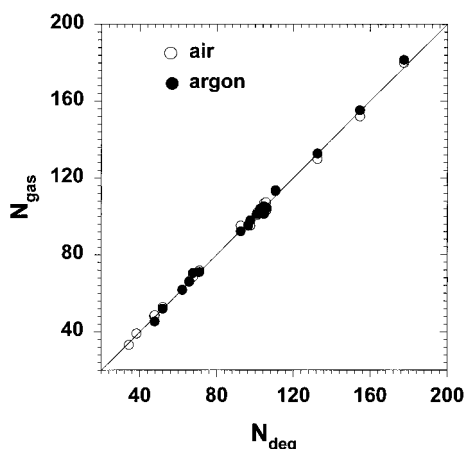
(26) Malliaris, A.; Binana-Limbélé, W.; Zana, R. *J. Colloid Interface Sci.* **1986**, *110*, 114.

(27) Binana-Limbélé, W. Doctorate Thesis, University Louis Pasteur, Strasbourg, France, June 1989.

Table 2. Aggregation Numbers, N , of Different Surfactants in Aqueous Solutions Determined in the Absence and in the Presence of Gas (Air and Argon)

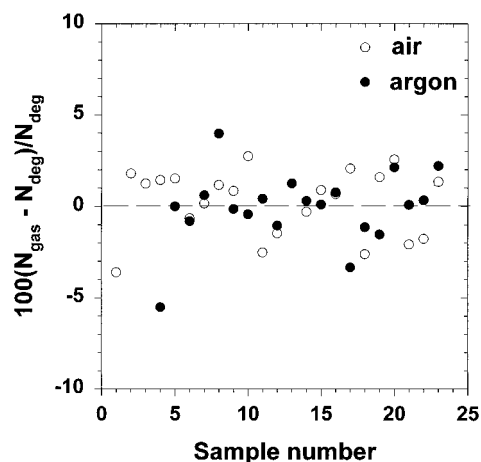
sample no.	surfactant	T (°C)	N_{air}	N_{deg}	N_{Ar}
1	0.108 M DTAC	35	33.2	34.4	
2	0.108 M DTAC	25	39.0	38.3	
3	0.108 M DTAC	10	48.1	47.5	
4	0.099 M $\text{C}_{12}\text{N}_3\text{CO}_2$	25	48.5	47.8	45.3
5	0.099 M $\text{C}_{12}\text{N}_3\text{CO}_2$	10	52.7	51.9	51.9
6	0.098 M BHDC	25	61.7	62.1	61.6
7	0.100 M $\text{C}_{12}\text{N}_3\text{SO}_3$	25	65.8	65.7	66.1
8	0.097 M SDS	25	68.5	67.7	70.5
9	0.100 M $\text{C}_{12}\text{N}_3\text{SO}_3$	10	71.6	71.0	70.9
10	0.097 M TTAB	25	95.1	92.5	92.1
11	0.072 M C_{12}E_8	10	95.1	97.5	97.9
12	0.106 M CTAC	30	95.0	96.4	95.4
13	3.44 wt% TX100 ^a	25		102.7	104.0
14	0.100 M CTAC	25	100.5	100.8	101.1
15	0.071 M C_{12}E_8	20	102.0	101.1	101.2
16	0.072 M C_{12}E_8	25	105.2	104.5	105.3
17	0.100 M CTAC	10	106.8	104.6	101.2
18	0.106 M CTAC	20	103.2	105.9	104.7
19	0.071 M C_{12}E_8	30	107.3	105.6	104.0
20	0.072 M C_{12}E_8	35	113.6	110.7	113.1
21	0.028 M C_{12}E_6	15	129.8	132.5	132.6
22	0.028 M C_{12}E_6	20	151.9	154.6	155.1
23	0.028 M C_{12}E_6	25	179.9	177.5	181.5

^a This solution was also measured after saturation with nitrogen and the measured aggregation number was found to be 104, which is very close to the values presented in the table.

**Figure 1.** Values of aggregation numbers measured in the presence of air (○) and argon (●) plotted against the aggregation numbers of the same solutions in the absence of dissolved gas.

reveals no systematic trend for the deaerated solutions with respect to the gas-saturated solutions. This is also apparent in Figure 1 where the values of N in the presence of gas (air or argon) are represented against the N values for the deaerated solutions. All data points follow the solid line of slope 1, with no systematic deviation from this line. Note that an increase in the temperature leads to a pronounced increase in the aggregation number of C_{12}E_6 micelles, which become elongated. Such micelles should be more sensitive to any change in composition of the surrounding medium. However, even for the largest nonionic micelles, the distances between the data points and the diagonal are not larger than those for the smaller micelles investigated.

Figure 2 is a plot of the relative differences between the aggregation numbers in the solutions saturated with air or argon and the fully deaerated ones. The data points for the air-saturated solutions (empty symbols) and for the argon-saturated ones (filled symbols) are about equally distributed around the horizontal line corresponding to a zero value of the difference. All values of the relative differences, but two, are smaller than 4%. The maximum experimental error on N can be taken as 5%.

**Figure 2.** Relative differences between the aggregation numbers determined with air-saturated (○) or argon-saturated (●) solutions and the aggregation numbers of the same solutions in the absence of dissolved gas.

The influence of butane, which is expected to dissolve to a greater degree in aqueous surfactant solutions than argon and air,²⁸ was checked with 0.1 M $\text{C}_{12}\text{N}_3\text{SO}_3$ at 25 °C (sample 7). The butane was introduced in the fluorescence cell containing the deaerated sample, and the system was left to equilibrate overnight. The aggregation number was found to be 65.3, which is a value very close to those listed for the same surfactant solution in Table 2.

The reproducibility of the experimental results was studied using 0.1 M CTAC solutions at 25 °C. Ten identical solutions (same content of pyrene and cetylpyridinium chloride) were prepared and separated into two equal groups. For one group the measurements were performed first with air-saturated solutions, then with completely deaerated solutions and finally after saturating them with argon. The solutions of the second group were studied in the order deaerated, argon-saturated, and air-saturated. For this purpose, the argon was removed using a vacuum pump, air was introduced inside the fluorescence cell, and the solutions were left overnight to equilibrate. A good measure for the state of saturation of the solution with air is provided by the value of the pyrene lifetime (see next section).

The values of aggregation numbers determined in the three states for all 10 solutions are presented in Figure 3 vs the sample number. Figure 4 shows the corresponding relative differences between the aggregation numbers in the presence of air or argon and in the absence of gas. The differences are smaller than 3% in all cases, i.e., even smaller than the maximum experimental error of about 5% found in the first series of experiments (see above). The numbers of full and empty symbols located on each side of the zero difference line are equal. The average values of N calculated for the samples in the presence of air and argon and in the absence of gas are respectively 100.5, 100.8, and 101.1. These results suggest that the effect of gas if any on the aggregation number of CTAC micelles at 25 °C is of less than 1%, which is well within the experimental error on such measurements, whichever the technique used.

Pyrene Fluorescence Lifetimes. As mentioned above, the lifetime of pyrene, τ , is strongly influenced by the presence of air because molecular oxygen is a very effective quencher of the pyrene fluorescence.²⁰ However,

(28) Bolden, P. L.; Hoskins, J. C.; King, A. D., Jr. *J. Colloid Interface Sci.* **1983**, *91*, 454 and references therein.

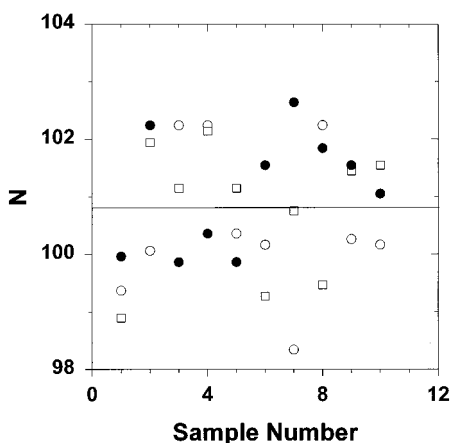


Figure 3. Values of the micelle aggregation numbers in 10 identical 0.1 M CTAC solutions at 25 °C, in the presence of air (○), saturated with argon (●) and in the absence of dissolved gas (□).

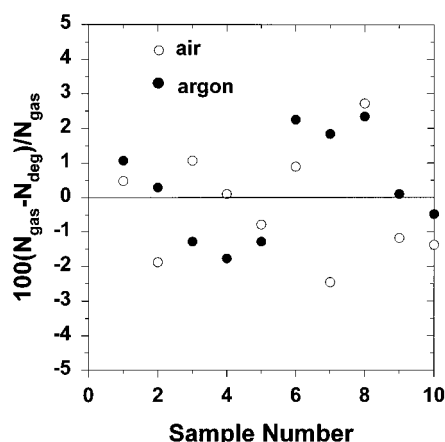


Figure 4. Micellar solutions of 0.1 M CTAC at 25 °C: relative differences between the aggregation numbers determined with air-saturated (○) or argon-saturated (●) solutions and the aggregation numbers of the same solution in the absence of gas. Solutions 1–5 were studied in the sequence air-saturated, deaerated, argon-saturated; solutions 6–10 were studied in the sequence deaerated, argon-saturated, air-saturated.

argon is not a quencher. Hence, one can easily distinguish between air-saturated solutions and deaerated and argon-saturated solutions. Also this sensitivity to molecular oxygen is a very strong argument in favor of the presence of gas within the micelles. The values of τ in different solutions are listed in Table 3. In all cases they are substantially smaller for air-saturated solutions than for the aerated or argon-saturated ones. As expected the values of τ for deaerated and argon-saturated solutions are the same, within the experimental error. The smallest difference between aerated and deaerated solutions is observed with the TTAB solution because the bromide ion is also an efficient quencher of the pyrene fluorescence.²⁰

Intramicellar Quenching Rate Constants. The intramicellar quenching rate constant k_q is proportional to the reciprocal of the viscosity, that is the fluidity, sensed by the probe and quencher in their motion in the micelle.^{19,29} Hence, the comparison of the values of k_q determined for air-saturated, degassed, and argon-saturated micellar solutions can be used to assess a possible effect of dissolved gas on the micelle viscosity or fluidity (also called microviscosity and microfluidity). The

Table 3. Values of Pyrene Fluorescence Lifetime, τ , for Different Surfactant Solutions, Determined in the Absence and in the Presence of Gas (Air or Argon)

sample no.	surfactant	T (°C)	$10^7\tau_{\text{air}}$ (s)	$10^7\tau_{\text{deg}}$ (s)	$10^7\tau_{\text{Ar}}$ (s)
1	0.108 M DTAC	35	1.496	3.125	
2	0.108 M DTAC	25	1.688	3.282	
3	0.108 M DTAC	10	2.232	3.526	
4	0.099 M $\text{C}_{12}\text{N}_3\text{CO}_2$	25	1.962	3.287	3.172
5	0.099 M $\text{C}_{12}\text{N}_3\text{CO}_2$	10	2.458	3.625	
6	0.098 M BHDC	25	1.765	3.523	3.494
7	0.100 M $\text{C}_{12}\text{N}_3\text{SO}_3$	25	2.097	3.429	3.481
8	0.097 M SDS	25	1.731	3.538	3.548
9	0.100 M $\text{C}_{12}\text{N}_3\text{SO}_3$	10	2.590	3.736	3.742
10	0.097 M TTAB	25	1.184	1.719	1.719
11	0.072 M C_{12}E_8	10	2.397	3.937	3.894
12	0.106 M CTAC	30	1.605	3.435	3.454
13	3.44 wt% TX100	25		3.129	3.225
14	0.100 M CTAC	25	1.796	3.509	3.526
15	0.071 M C_{12}E_8	20	2.497	3.707	3.732
16	0.072 M C_{12}E_8	25	1.997	3.678	3.664
17	0.100 M CTAC	10	2.357	3.793	3.759
18	0.106 M CTAC	20	1.941	3.641	3.592
19	0.071 M C_{12}E_8	30	2.164	3.577	3.563
20	0.072 M C_{12}E_8	35	1.632	3.522	3.511
21	0.028 M C_{12}E_6	15	2.511	3.725	3.791
22	0.028 M C_{12}E_6	20	2.197	3.444	3.468
23	0.028 M C_{12}E_6	25	1.899	3.011	3.071

Table 4. Values of Intramicellar Quenching Rate Constants, k_q , for Different Surfactant Samples, Determined in the Absence and in the Presence of Gas (Air or Argon)

sample no.	surfactant	T (°C)	$10^{-7}k_{q,\text{air}}$ (s)	$10^{-7}k_{q,\text{deg}}$ (s)	$10^{-7}k_{q,\text{Ar}}$ (s)
1	0.108 M DTAC	35	5.580	6.001	
2	0.108 M DTAC	25	4.250	4.152	
3	0.108 M DTAC	10	2.310	2.323	
4	0.099 M $\text{C}_{12}\text{N}_3\text{CO}_2$	25	2.704	2.714	2.560
5	0.099 M $\text{C}_{12}\text{N}_3\text{CO}_2$	10	1.553	1.493	1.559
6	0.098 M BHDC	25	0.600	0.575	0.572
7	0.100 M $\text{C}_{12}\text{N}_3\text{SO}_3$	25	1.748	1.858	1.762
8	0.097 M SDS	25	2.987	3.144	3.098
9	0.100 M $\text{C}_{12}\text{N}_3\text{SO}_3$	10	0.900	0.909	0.890
10	0.097 M TTAB	25	1.364	1.349	1.361
11	0.072 M C_{12}E_8	10	0.447	0.425	0.436
12	0.106 M CTAC	30	1.411	1.345	1.304
13	3.44 wt% TX100	25		0.437	0.429
14	0.100 M CTAC	25	1.214	1.131	1.107
15	0.071 M C_{12}E_8	20	0.623	0.624	0.624
16	0.072 M C_{12}E_8	25	0.737	0.738	0.725
17	0.100 M CTAC	10	0.590	0.605	0.620
18	0.106 M CTAC	20	0.907	0.872	0.896
19	0.071 M C_{12}E_8	30	0.833	0.827	0.835
20	0.072 M C_{12}E_8	35	0.967	0.935	0.946
21	0.028 M C_{12}E_6	15	0.411	0.405	0.422
22	0.028 M C_{12}E_6	20	0.372	0.362	0.393
23	0.028 M C_{12}E_6	25	0.331	0.318	0.339

k_q values are listed in Table 4 and Figure 5 shows the plot of the k_q values determined in the air-saturated and argon-saturated solutions as a function of the k_q values in the deaerated solutions. Again all the data points are very close to the straight line of slope unity (diagonal), and for a given solution, the differences between the different states of the solution are within the experimental error. Hence, the micellar microviscosity as reflected by the values of the intramicellar rate constant k_q appears to be independent of the presence or absence of solubilized gas.

Polarity Sensed by Pyrene at Its Solubilization Site. Table 5 lists the values of the ratio I_1/I_3 measured for some of the samples presented in Table 2. The results show practically the same values of I_1/I_3 (within the experimental error) in the three states for a given solution.

The agreement between the values determined in the presence and in the absence of dissolved gas is demonstrated in Figure 6. All points are distributed around and close to the diagonal. For most of the points the calculated relative differences between the values of I_1/I_3

(29) Lianos, P.; Lang, J.; Strazielle, C.; Zana, R. *J. Phys. Chem.* **1982**, 89, 1019.

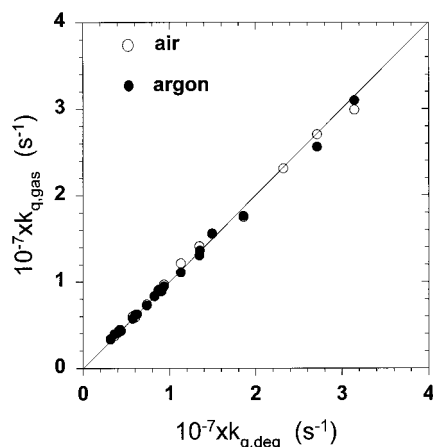


Figure 5. Plot of the values of the intramicellar quenching rate constant, k_q , obtained for air-saturated (○) and argon-saturated (●) solutions against the rate constant obtained for the same solutions in the absence of dissolved gas.

Table 5. Values of Pyrene Polarity Ratio, I_1/I_3 , for Different Samples in the Absence and in the Presence of Gas (Air or Argon)

sample no.	surfactant	T (°C)	I_1/I_3 (air)	I_1/I_3 (deg)	I_1/I_3 (Ar)
2	0.108 M DTAC	25	1.433	1.44	
3	0.108 M DTAC	10	1.471	1.485	
4	0.099 M C ₁₂ N ₃ CO ₂	25	1.476	1.478	1.475
5	0.099 M C ₁₂ N ₃ CO ₂	10	1.54	1.535	1.531
6	0.098 M BHDC	25	1.34	1.338	1.338
7	0.100 M C ₁₂ N ₃ SO ₃	25	1.436	1.443	1.44
8	0.097 M SDS	25	1.166	1.156	1.188
9	0.100 M C ₁₂ N ₃ SO ₃	10	1.485	1.486	1.482
10	0.097 M TTAB	25	1.379	1.375	1.375
11	0.072 M C ₁₂ E ₈	10	1.31	1.309	
14	0.100 M CTAC	25	1.374	1.375	1.372
16	0.072 M C ₁₂ E ₈	25	1.264	1.257	1.257
17	0.100 M CTAC	10	1.429	1.427	1.421
20	0.072 M C ₁₂ E ₈	35	1.169	1.192	

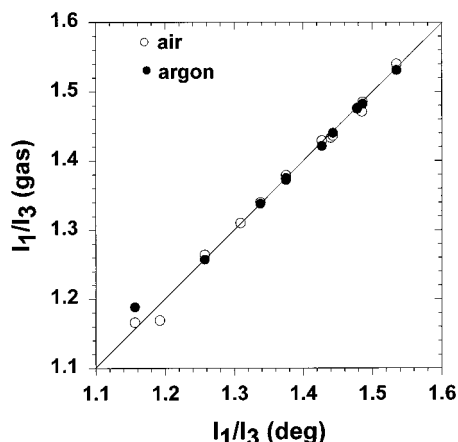


Figure 6. Plot of the values of the pyrene polarity ratio, I_1/I_3 , for the air-saturated (○) and argon-saturated (●) solutions listed in Table 5, against the value of the ratio obtained for the same solutions in the absence of dissolved gas.

in the presence of air or argon and in the deaerated samples are below 1%.

Concluding Remarks

The present study examined the micelle aggregation numbers and also the micelle microviscosity and micropolarity of different ionic, nonionic, and zwitterionic surfactants in aqueous solutions saturated with air or argon and completely deaerated. Overall, the measurements involved some 33 systems. The micelle aggregation number, the microviscosity, and the micropolarity were

found to be independent of the presence or absence of solubilized gas and of its nature, within the experimental error of the measurements. It may be argued that for the ionic micelles investigated the large counterion concentration in the vicinity of the micelle surface (up to 4 M) reduces much the gas concentration at the micelle surface and thus results in a negligible effect of the solubilized gas on the micellar properties. However, the large effect of molecular oxygen on the pyrene lifetime is a strong argument in favor of transient contacts between oxygen, and likely of any other solubilized gas introduced in the micellar solution, and micelle-solubilized pyrene. That is oxygen or any other solubilized gas will very easily penetrate and exit the micelles as shown by Almgren et al.³⁰ Besides, the solubilization of gases by micelles is experimentally well-established,^{10–12,28} and the solubility of gases in oil-like materials compounds, similar to the micelle interior, is larger than in water.³⁰ Also the effect of solubilized gas was found to be negligible for the nonionic and the zwitterionic surfactant solutions investigated which contain no counterions. It can therefore be safely concluded that the effect of gas, if any, must be extremely small, below 1% in the case of the value of the aggregation number, as indicated by our results for the series of solutions of cetyltrimethylammonium chloride. In turn, one is led to the conclusion that the hydrophobic interaction involved in the formation of micelles is not affected by the presence of dissolved gas in the system. Indeed, the aggregation number is an exponential function of the free energy ΔG_t for the transfer of one surfactant from the aqueous phase to the micelles.^{1,2} For a surfactant with a dodecyl chain, the contribution of the hydrophobic interaction to ΔG_t would be about 15 kT.³¹ Attributing a possible effect of gas to a change of the hydrophobic contribution to ΔG_t , a change of N by 1% corresponds to an absolute change of this contribution by 0.01 kT and a relative change of less than one part per thousand, a very small effect indeed. Note that there has been a very careful study of the index of refraction of thin aqueous films confined between hydrophobic surfaces in order to try to detect microbubbles of gas that have been postulated to be responsible for the long-range hydrophobic interaction between surfaces.³² This study did not detect such bubbles, within the limitation of its sensitivity.

Note Added in Proof. A Reviewer of this work pointed out that the solubility of oxygen and air in water being in the millimolar range (see ref 30), there is on average less than one oxygen molecule per micelle in a typical micellar solution of surfactant. On this basis, and reported results about the effect of alkanes on the value of the SDS micelle aggregation number,³³ one should not expect any effect of solubilized gases, as our measurements indicated.

Acknowledgment. The authors thank Pr. B. Ninham (Lund, Canberra) and Dr. P. Kékicheff (Strasbourg) for helpful discussions and critical reading of the manuscript. R.A. and I.K. thank Professors Ivanov and Krachelsky for allowing them to perform this work in Strasbourg. The financial support received under the European program Tempus JEP 09789-95 is gratefully acknowledged.

LA971008Y

(30) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188.

(31) Mukerjee, P. *Adv. Colloid Interface Sci.* **1967**, *1*, 241.

(32) Kékicheff, P.; Spalla, O. *Langmuir* **1994**, *10*, 1584.

(33) Almgren, M.; Swarup, S. *J. Phys. Chem.* **1982**, *86*, 4212.