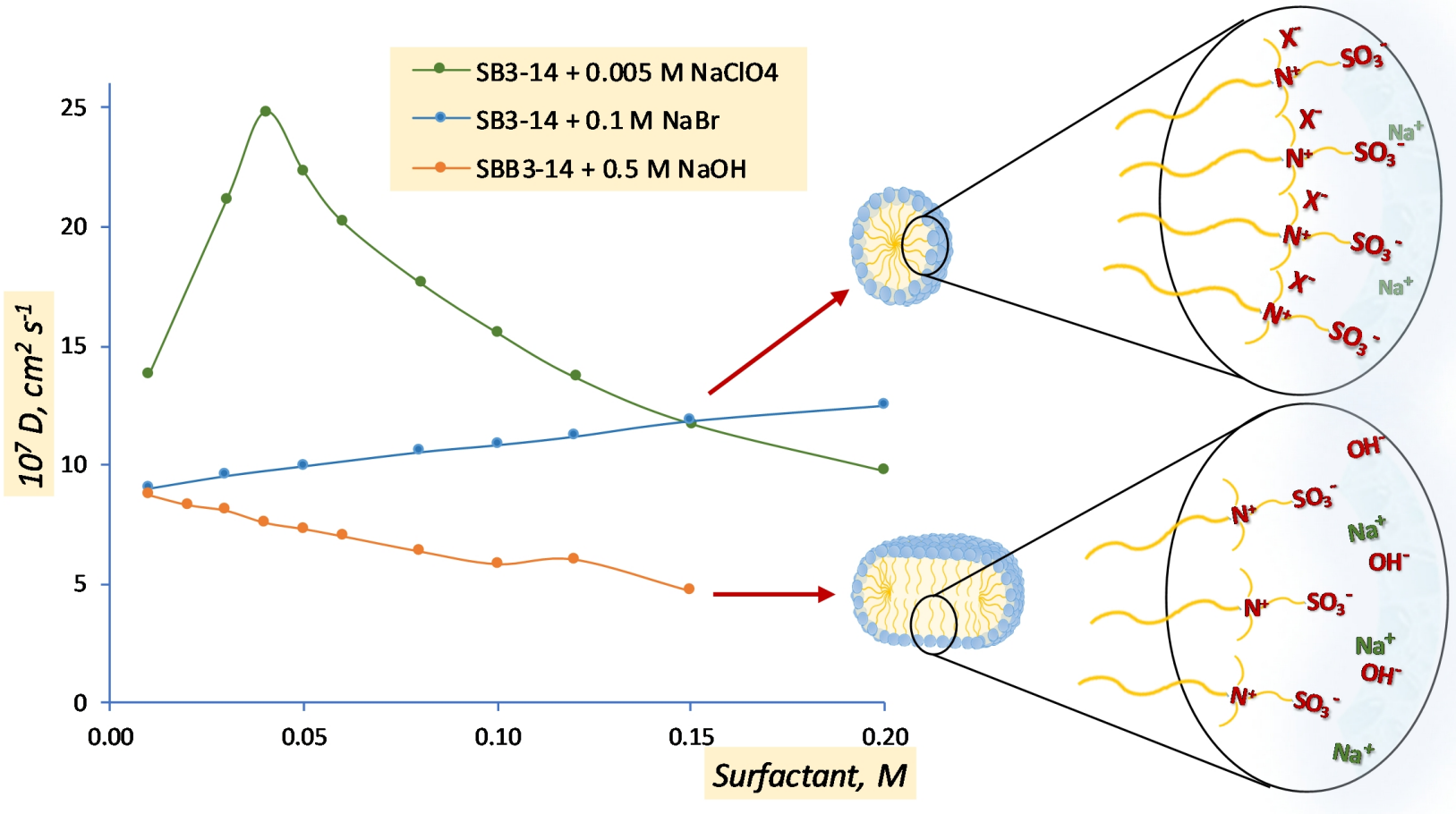

SB3-14 + 0.005 M NaClO4
SB3-14 + 0.1 M NaBr
SBB3-14 + 0.5 M NaOH
10^7 D, cm^2 s^{-1}
25
20
15
10
5
0
0.00
0.05
0.10
0.15
0.20
Surfactant, M
X-
N+
SO3-
Na+
OH-

Surface charge modulation of sulfobetaine micelles by interaction with different anions: A dynamic light scattering study

P. Di Profio,*[a,b] R. Germani,[b,c] A. Fontana,[a] V. Canale[a]

[a]*Department of Pharmacy, University of Chieti-Pescara "G. d'Annunzio"*

[b]*CEMIN - Center of Excellence on Nanostructured Innovative Materials, University of Perugia*

[c]*Department of Chemistry, Biology and Biotechnology, University of Perugia*

*Corresponding Author: Pietro Di Profio, Department of Pharmacy, University of Chieti-Pescara "G. d'Annunzio", via dei Vestini 31, I-66100 Chieti (Italy); e-mail: pietro.diprofio@unich.it. Orcid ID: 0000-0002-8038-7940

Keywords: Zwitterionic Surfactants; Micelles; Head-group hydrophobicity; Dynamic light scattering; DLVO; Specific interactions.

Abbreviations: dynamic light scattering (DLS); critical micelle concentration (cmc); tetradecyl dimethylammonium propanesulfonate (SB3-14); tetradecyl diethylammonium propanesulfonate (SBE3-14), tetradecyl dipropylammonium propanesulfonate (SBP3-14); tetradecyl dibutylammonium propanesulfonate (SBB3-14); diffusion coefficient (D); hydrodynamic radius (R_h); coefficient of variation (CV). Lines connecting data points in Figures 2-11 are meant as a guide for the eye only.

ABSTRACT

This work reports a Dynamic Light Scattering study on aqueous micelles formed by tetradecyl dialkylammonium propanesulfonate surfactants (sulfobetaines; with alkyl = methyl, ethyl, *n*-propyl and *n*-butyl) within a range of surfactant concentrations (0.01 - 0.40 M) both in pure water and in the presence of various concentrations of NaBr, NaOH and $NaClO_4$ (0.02 - 0.50 M NaBr; 0.10 - 1.00 M NaOH; 0.005-0.50 M $NaClO_4$). From values of diffusion coefficients, D, we obtained micellar hydrodynamic radii, R_h, by application of the Stokes-Einstein relation. Plots of D vs. sulfobetaine concentrations can be qualitatively explained with a model based on a linear interaction theory, which allowed to separate thermodynamic and hydrodynamic perturbations to D. Results show that: i) formally neutral sulfobetaine micelles become negatively charged by preferential interaction with strongly interacting, "soft" anions; ii) the surface negative charge increases with the hydrophobicity of the anions; iii) bulkier alkyl substituents on the sulfobetaine head groups lead to less charged, less hydrated aggregates, which result in opposite perturbations to D; (iv) highly hydrated, high charge density hydroxide ions lead to an increase of micellar sizes through a disc-like growth pattern.

1. INTRODUCTION

Zwitterionic surfactants represent one of the most interesting families of self-organizing molecules. While being formally neutral, their micelles may have a positive or negative electrostatic charge depending on the degree of differential interaction with cations and anions added to micellar solution.[1–5] In general, they show high compatibility with inorganic and organic ions, and exhibit high solubility in water and aqueous electrolyte solutions.[6] Betaines are compatible with all other classes of surfactants and lipids, except for low pH anionics;[7–9] they also show excellent chemical stability against oxidizing agents and extreme pH values, and have been studied with the aim of performing chiral recognition.[10] The critical micellar concentration (cmc) of these compounds is quite low (10^{-5} - 10^{-4} M).[11] Betaines and sulfobetaines also have significant functional properties, for example as foaming agents, wetting agents and emulsifiers, particularly suitable for use in "hard" aqueous systems.[12,13] Sulfobetaines have been recently tested as gas hydrate inhibitors in a chemoinformatic modeling study,[14] as promoters in the separation of model biogas mixtures,[15,16] and under hydrogel form in the dispersion of catalysts based on carbon nanotubes.[17,18]

A fundamental functional feature of these species is the low irritation potential to human skin, which makes them components of choice in personal care products.[19] Another interesting feature is that micellar aggregates formed by zwitterionic amphiphiles constitute a simple model of biological membranes. In particular, information obtained from the study of those models can be related to the relationship and interactions of cell surfaces with various ionic species. It is known that the physical properties of aqueous solutions of surfactants are sensitive to the chemical nature of added ions. Br^- or ClO_4^- anions interact by means of both specific and Coulombic effects, staying close to the micellar interface. Such behavior is typical of “soft” counterions, characterized by high polarizability and low charge density (chaotropic anions). Other ions, such as OH^-, F^- or $HCOO^-$ (cosmotropic anions) are strongly hydrated, and interact with the surfactant headgroups only by means of a Coulombic

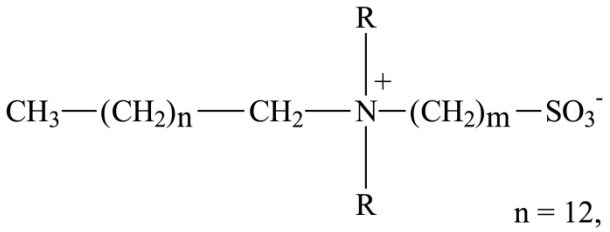
interaction, being located in the outer region of the micellar interface. The degree of ion association is related to its charge density and degree of hydration, following the Hofmeister series. [20–25]

The present paper reports a dynamic light scattering (DLS) characterization of aqueous micelles formed by sulfobetaines with different alkyl moieties on the head group nitrogen (Figure 1) in the presence of various concentrations of NaBr, NaOH and $NaClO_4$. DLS allowed to estimate the interaction behaviour of zwitterionic micelles with anions of different sizes and hydration shell, and showed that large, polarizable anions (Br^-, ClO_4^-) interact more strongly than OH^- with the ammonium cation, as widely reported in the literature,[3,5,6,26] thus providing a net negative charge to the micellar aggregate. Remarkably, diffusion coefficients (*D*) profiles show with unprecedented clarity the saturation of the ammonium layer by perchlorate anions. Interaction with hydroxide ions lead to micellar growth, possibly with oblate spheroid geometry. Overall, the present results form a phenomenological framework of the interaction of different anions and homolog members of a sulfobetaine family, also showing novel non-monotonic behaviours in case of very strong interactions.

2. MATERIALS AND METHODS

2.1 Chemicals

Figure 1 reports the general formula for sulfobetaine surfactants used in this work. SB3-14 was from Sigma-Aldrich, and was recrystallized from 3/1 acetone/methanol before use. SBE3-14, SBP3-14, and SBB3-14 were prepared from propane sultone and the corresponding tertiary amines, as described.[3] Values of critical micelle concentrations, *cmc's*, were determined from plots of surface tension vs -log[surfactant], showing no minima, on a Fisher, du Nouy type, tensiometer at room temperature in deionized, bidistilled water. Cmc's are: SB3-14, $2.9 \cdot 10^{-4}$M; SBE3-14, $2.6 \cdot 10^{-4}$M; SBP3-14, $2.0 \cdot 10^{-4}$M; SBB3-14, $9.6 \cdot 10^{-5}$M.



n = 12, m = 3, R = Me: **SB3-14**

n = 12, m = 3, R = Et: **SBE3-14**

n = 12, m = 3, R = n-Pr: **SBP3-14**

n = 12, m = 3, R = n-Bu: **SBB3-14**

Figure 1. Structure of sulfobetaines investigated in the present work.

2.2 Dynamic Light Scattering

Sample solutions were prepared using MilliQ water, which was filtered through 0.2 μm polycarbonate filters (Millipore). 1 mL of sample was filled into a 6 mm glass tube, protected from dust by Parafilm caps, and centrifuged at 10000 rpm for 15 min to sediment dust particles. The glass tube was fitted into a toluene-filled fluorimeter cuvette to provide refractive index matching. The cuvette was placed into a thermostatted aluminum cell, which was regulated to ± 0.05°C. Laser light was from a Coherent Innova 70-3 argon-ion laser operating at 4880 Å. Light scattered at 90° was focused onto the slit of a photomultiplier tube (Products for Research, Inc., USA). A 64-channel Nicomp Model 370 computing autocorrelator (PSS, Santa Barbara, USA) was used to calculate and display the diffusion coefficient, *D*, and derived parameters from cumulants analysis to the intensity autocorrelation function.[27] All measurements showed values of chi-squared and fit error (see Supplementary) close to 1, and coefficients of variation (CVs) were typically below 20%, thus pointing to a general monodispersity of micelle sizes, except where noted (see Supplementary Material). An exception to this general finding was observed under high sulfobetaine concentrations in the presence of perchlorate ions, where CVs were around 30-40%.

Generally, intermicellar interactions as revealed by the slopes of diffusivity profiles have been treated in terms of the theory of linear interaction, as extensively described in the literature.[28–31] Here, we limit our qualitative treatment to a few relations that can help with the following Discussion and

Conclusions. The micellar diffusivity, D, in dilute surfactant aqueous solutions varies linearly as a function of the micellar volume fraction, ϕ:

$$D = D_0 [1 + (K_t + K_h)\phi] \qquad (1)$$

In eq. (1), D_0 represents the diffusivity at infinite dilution (critical micelle concentration, cmc), where intermicellar interactions are negligible. K_t and K_h are thermodynamic and hydrodynamic correction coefficients,[32] where K_t is proportional to the second virial coefficient, and can be written as:[33]

$$K_t = 8 + 24\int_0^\infty dx(1+x)^2[1-e^{-W(x)/kT}] \qquad (2)$$

where x is the intermicellar separation parameter ($x = (r - 2a)/2a$, where a = particle radius, r = separation between particles). The numerical term, 8, in eq. (2) is the value for the hard-sphere interaction. Hydrodynamic perturbations can be written in a similar form:[34]

$$K_h = -6.44 - \int_0^\infty dxF(x)[1-e^{-W(x)/kT}] \qquad (3)$$

where $F(x)$ is a polynomial function of x (cf. above).

Similarly, in eq. (4), the numerical term (-6.44) is the contribution for hard-sphere interactions. The negative sign refers to the hydrodynamic correction being opposed to the thermodynamic one, thus "slowing down" the particle diffusivity. For interacting species (e.g., micellar aggregates), K_h and K_t also contain contributions from micellar surface charge repulsions $W_R(x)$, and an attractive, van der Waals potential $W_A(x)$. A full derivation of those potentials for ionic micelles is described in the literature.[28,29,34–36] In particular, the repulsive part of the interaction potential (W_R) contains the ionic strength of the solution, I, through the Debye-Hückel inverse screening length, κ:

$$\kappa = [8\pi I e^2/(\varepsilon kT)]^{1/2} \qquad (4)$$

where ε is the T-dependent solvent dielectric constant, and e is the charge of the electron.

To our knowledge, application of the linear interaction-DLVO theory to zwitterionic micelles in the presence of interacting ions has not been attempted in the literature, even if this should be possible by simply considering the fact that, overall and without going into detail, the ionic strength of zwitterionic micellar solutions should *decrease* with surfactant concentration, instead of *increasing*, as modelled with ionic micelles. This decrease is obviously due to the uptake of ions (particularly, anions) by the surface ammonium cations of the micelle.

The micellar radius can be approximated to the hydrodynamic radius, R_h, which is estimated by applying the Stokes-Einstein relation to the common intercept, D_0, of diffusivity profiles in the limit of vanishing surfactant concentration:

$$R_h = kT/6\pi\eta D_0 \qquad (5)$$

where η is the shear viscosity of the solution (H_2O + salt).

2.3 Zeta potential measurements

Zeta potentials of some selected samples were made with a Brookhaven Zeta-PALS. The settings of the instrument were verified by measuring a standard latex particle sample with a zeta potential of -69 ± 6 mV. Samples were run in triplicate, and results with standard deviation below 15% were averaged.

2.4 Zeta potential measurements

Rheological properties were evaluated using a Haake M.A.R.S. II Thermo Scientific modular rheometer provided with a cone-plate system (diameter of 60 mm and cone angle of 0.5°), a thermo-controller apparatus Haake Phoenix (Thermo Electron Corporation), and a RheoWin software 3.61 (Thermo Fisher Scientific) for data elaboration. Rheological tests were performed using a fixed gap

of 0.026 mm. Analyses in dynamic mode were carried out to estimate both the storage (G') and the loss (G") moduli from 0.01 to 10 Hz.[37]

3. RESULTS AND DISCUSSION

3.1. No added salts/Added NaBr

DLS experiments were carried out on aqueous micellar systems formed by SB3-14, SBE3-14, SBP3-14 and SBB3-14 both in water with no added ions and in aqueous solutions of NaBr, NaOH and $NaClO_4$. Micellar solutions of these sulfobetaines are generally homogeneous (clear) in a wide range of surfactant and salt concentrations, thus macroscopically suggesting the existence of a substantial balance between repulsive and attractive intermicellar interactions under a wide range of conditions. The interpretation of repulsive terms for globally neutral surfaces of zwitterionic colloids in the absence of added electrolytes is not straightforward. On the other hand, it has been widely reported that differential association of anions with the ammonium moieties of the micellar surface lead to a surface negative charge which makes the zwitterionic micelles anionic.[1–3,5,6,26,38–40]

The diffusivity profile for SB3-14 micelles in water is approximately linear and shows a slightly negative slope (Figure 2). The R_h value, as obtained by extrapolating the profile to the cmc, is 2.70 nm. The situation is qualitatively similar for SBE3-14, SBP3-14 and SBB3-14 (Figures 3-5), and analysis of R_h values shows a modest decrease in micellar size when increasing the size of alkyl residues (Table 1).

Table 1: Values of D_0 and R_h extrapolated to [T] = 10^{-4} M for diffusivity profiles at 25.0°C in water and in NaBr aqueous solutions. $\Delta D_{0(\max)}$ is a measure of maximum deviation from a common intercept.

Surfactant	[NaBr], M	10^7 D_0, cm^2 s^{-1}	R_h, nm	$\Delta D_{0(\max)}$

SB3-14	0.00	9.07	2.70	ca. 7%
	0.02	9.36	2.62	
	0.10	9.00	2.73	
	0.50	8.80	2.79	
SBE31-4	0.00	9.16	2.68	ca. 14%
	0.02	9.76	2.51	
	0.10	8.76	2.80	
	0.50	8.59	2.86	
SBP3-14	0.00	9.37	2.62	ca. 3%
	0.02	9.19	2.67	
	0.10	9.23	2.66	
	0.50	9.11	2.69	
SBB3-14	0.00	10.35	2.37	ca. 14%
	0.02	9.46	2.59	
	0.10	9.31	2.63	
	0.50	9.17	2.67	

This apparent size decrease has been observed previously with fluorescence quenching experiments,[3] can be tentatively explained by recalling that the hydrodynamic radius, as obtained from the Stokes-Einstein relationship, relates to the size of the aggregate with its surface hydration sphere. An increase in the hydrophobic character of the micellar surface, as the alkyl groups become bulkier, leads reasonably to a decrease in the number of water molecules that "move" together with the aggregate, and consequently to a decrease in R_h.

The addition of NaBr to sulfobetaine solutions dramatically changes their observed behavior. For SB3-14, SBE3-14 and SBP3-14, all *D* profiles with added salts have a positive slope (Figures 2-4), and there is a slight deviation from linearity only for [NaBr] = 0.02 M. For SBB3-14, there is a negative slope also for the lower salt concentration (Figure 5). By increasing the amount of sodium bromide, profiles shift to a slightly positive slope which is not greatly affected by a further increase in ionic strength.

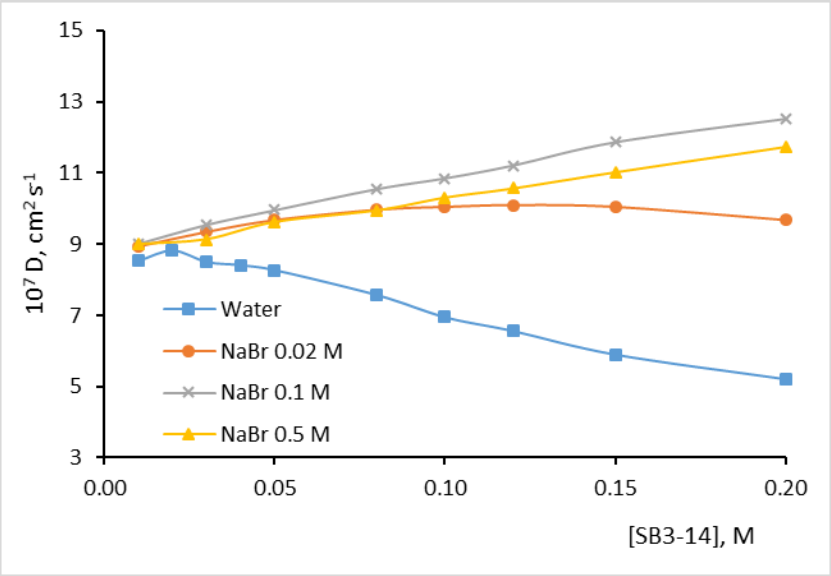


Figure 2: Diffusivity profiles for SB3-14 in water and different concentrations of NaBr at 25.0°C.

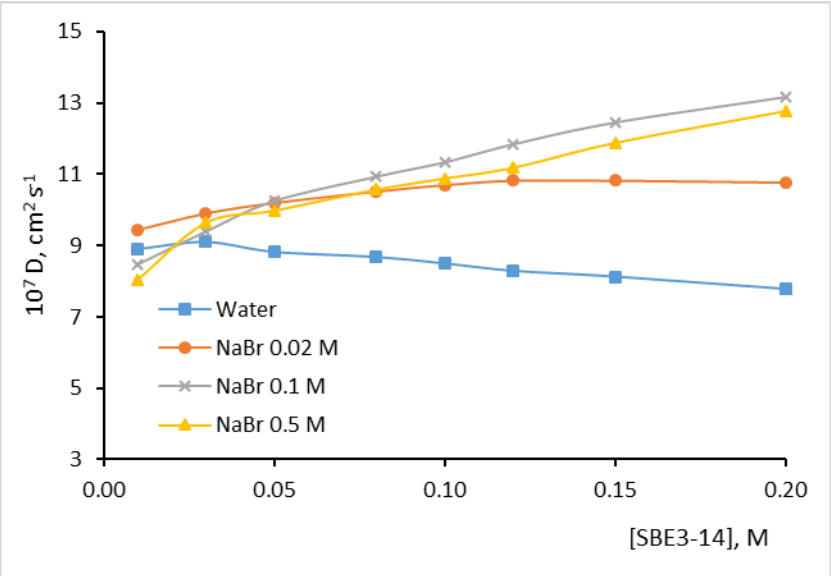


Figure 3: Diffusivity profiles for SBE3-14 in water and different concentrations of NaBr at 25.0°C.

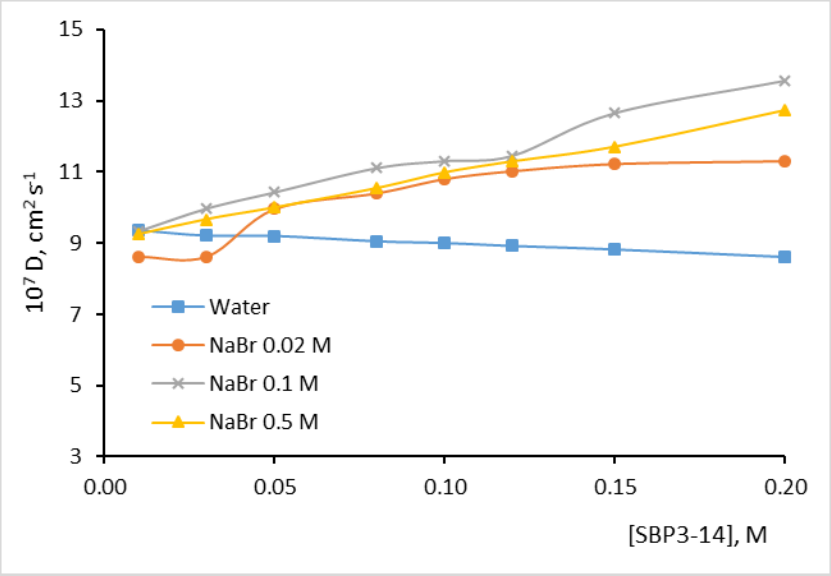


Figure 4: Diffusivity profiles for SBP3-14 in water and different concentrations of NaBr at 25.0°C.

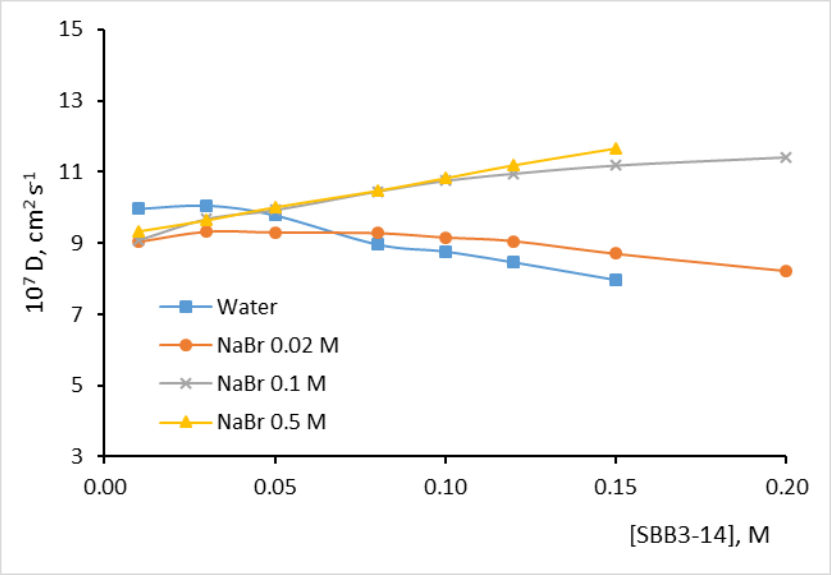


Figure 5: Diffusivity profiles for SBB3-14 in water and different concentrations of NaBr at 25.0°C.

Qualitatively, one may surmise that the association of soft, poorly hydrated Br^- ions with ammonium moieties of the surfactants is stronger than those of Na^+ with sulfonate groups, giving rise to the formation of a net negative charge on the micellar surface. Then, micelles begin to show electrostatic repulsions leading to an increase in positive slopes. As a confirmation of this known behaviour, Zeta potential (ZP) values for SB3-14 in 0.1 M NaBr become increasingly less negative when going from

0.05 M SB3-14 (ZP = -30.6 mV) to 0.15 M SB3-14 (ZP = -15.0 mV). following a further increase of NaBr concentrations, a growing fraction of the electrolyte remains in the aqueous pseudo-phase, thus increasing the ionic strength which leads to a more effective shielding of repulsions, and hence a levelling of slopes. The "anomalous" (i.e., slightly negative) slope of SBB3-14 with 0.02M NaBr can be explained by a reduced binding of bromide anions due to the presence of a more hydrophobic environment around the ammonium moieties, and consequently a lower surface charge of SBB3-14 micelles.

One can discuss whether there is a common intercept of diffusivity profiles extrapolated at the cmc, which is usually taken as a good indication of the absence of micellar growth.[41] From Table 1, it is noted that the differences in extrapolated values for each sulfobetaine (ΔD_0 (max)) in water and in NaBr solutions are at most 14%; in other words, if the observed differences are real, it must be concluded that the addition of NaBr causes only a modest increase in aggregate sizes. It should be added, however, that at low surfactant concentration scattered intensities are low, and the experimental error is of the same order as the observed differences.

3.2. NaOH

Quite different profiles are obtained when the electrolyte is NaOH (Figures 6-9). Diffusivity values are almost overlapping for SB3-14 up to 1M NaOH, and very close to those in water (Figure 6). This behaviour seems to indicate either (i) a substantial lack of interaction of hydroxide and sodium ions with ammonium and sulfonate groups, respectively, or (ii) interactions taking place with nearly equal binding affinities, leading to the same overall effect as (i). As the size of the head group increases, however, more concentrated NaOH solutions lead to a progressive increase in negative slopes without increasing the DLS coefficients of variation, which indicates nearly monodisperse micellar populations throughout the explored (salt and sulfobetaine) concentration ranges (see tables 6-8 in Supplementary Material). This finding may suggest an effective growth of aggregates, especially with

SBB3-14, which shows the most pronounced effects, and an obvious lack of a common intercept at the cmc (Figure 9).

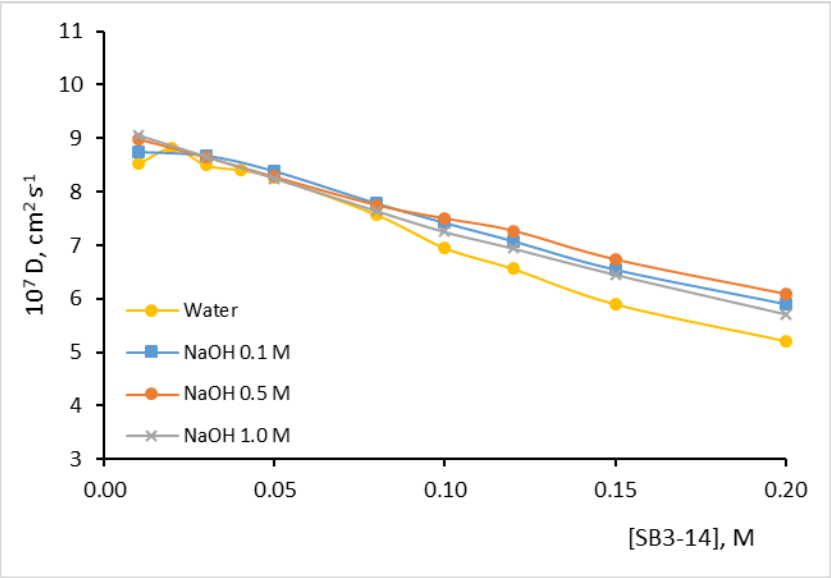


Figure 6: Diffusivity profiles for SB3-14 in water and different concentrations of NaOH at 25.0°C.

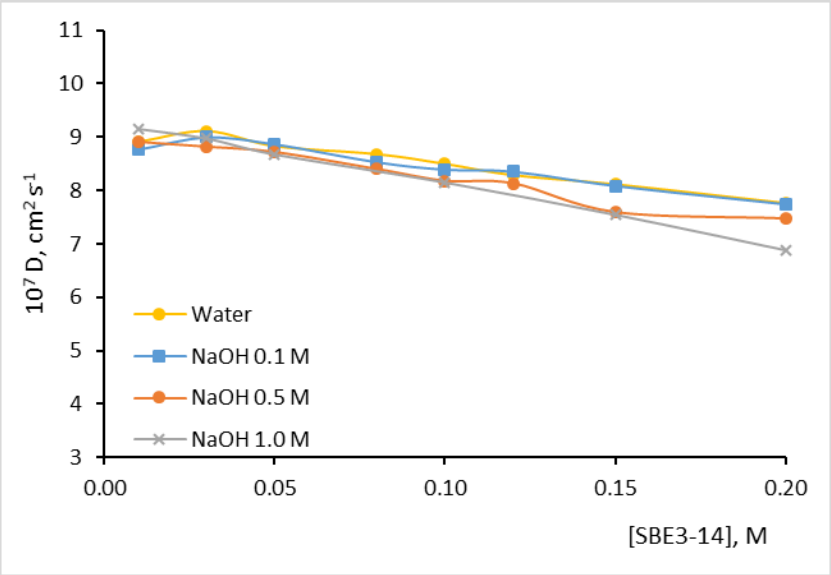


Figure 7: Diffusivity profiles for SBE3-14 in water and different concentrations of NaOH at 25.0°C.

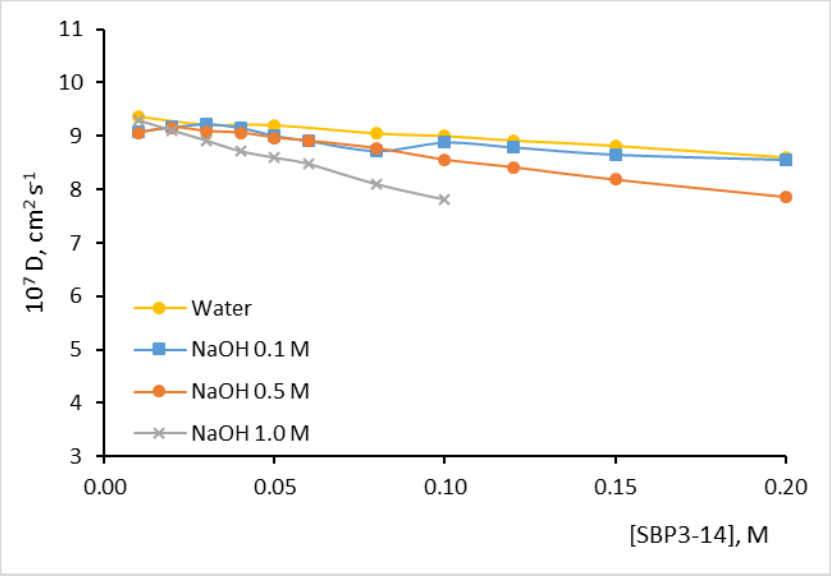


Figure 8: Diffusivity profiles for SBP3-14 in water and different concentrations of NaOH at 25.0°C.

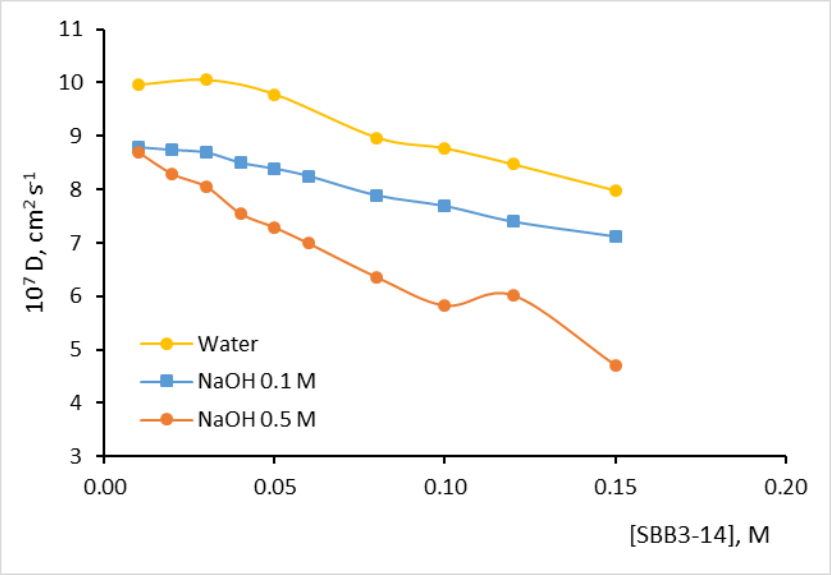


Figure 9: Diffusivity profiles for SBB3-14 in water and different concentrations of NaOH at 25.0°C.

The difference in viscoelastic properties of SBB3-14 in water and 0.5 M NaOH, where most pronounced growth effects were observed, were studied under dynamic shear conditions, and values of G' and G" moduli are summarized in Table 2. It was observed that G', which is related to the elastic behaviour of the sample, increased from 17.9 x 10^{-3} Pa to 40.8 x 10^{-3} Pa for 0.5 M NaOH / 0.05 M

SBB3-14. These results could possibly hint to the formation of aggregates larger than those found for 0.05 M SBB3-14 in water, without giving any information on the shape of the aggregates.[42]

Table 2. Rheological parameters of SBB3-14 formulations.

	SBB3-14 0.05 M	**SBB3-14 0.05 M + NaOH 0.5 M**
G' (Pa)	17.87×10^{-3}	40.79×10^{-3}
G" (Pa)	23.47×10^{-3}	15.43×10^{-3}

We may then try to find a model for micellar growth which takes into account the observed size monodispersity. Fluorescence quenching experiments[3] show a modest increase (23%) of aggregation numbers (*N*) for SBP3-14 in 0.1M NaOH, where our DLS data show no major differences as compared to *D* profiles of SBP3-14 in water (Fig. 8). At the best of our knowledge, no data are known from the literature regarding the variation of sulfobetaine micelle aggregation numbers in the presence of high concentrations of hydroxide ions. Hybrid simulations using molecular dynamics coupled to self-consistent field theory (MD-SCF), as applied to Triton X-100, show that micelles with low *N* (ca. 40) are spherical, while those with $N > 140$ are essentially prolate ellipsoids. Intermediate N values (around 70) are compatible with oblate or disc-like ellipsoids.[43] A micellar growth model according to a prolate or rod-like geometry should entail a remarkable increase of polydispersity,[44] as was also found experimentally.[45,46] This can be explained on the basis that the addition of surfactant monomers to a growing rod-like micelle will only increase its long axis (one-dimensional growth), then there won't be major energy differences among rods containing *N*, *N*+1, …, *N*+n surfactant monomers, this leading to a large polydispersity of the micellar population. On the other hand, a micellar growth towards an oblate or disc-like shape should be possible with no or little increase in polydispersity, given the more stringent geometric requirements. In fact, if we add a surfactant monomer to a growing oblate micelle, this addition will result in a 2-dimensional

enlargement of the quasi-planar region of the discoidal aggregate, as opposed to the one-dimensional growth of rods. On a more quantitative basis, we can adopt a simple symbolism as applied to generic prolate or oblate aggregates,[44] and introduce the dependence of the chemical potential of surfactant micellization on the aggregation number of the micelle. If we define μ_N^0 as the mean interaction free energy per surfactant molecule in an aggregate of aggregation number N, we can state that an aggregate will form when μ_N^0 decreases with N. It is also known that, to a first approximation, the dependence of μ_N^0 on N is determined by the geometrical shape of the aggregate. Therefore, for a rod-like (prolate) micelle, we can write:

$$\mu_N^0 = \mu_\infty^0 + \alpha kT/N \qquad (6)$$

whereas, for a disc-like (or oblate) micelle,

$$\mu_N^0 = \mu_\infty^0 + \alpha kT/N^{1/2} \qquad (7)$$

where μ_∞^0 is the energy of a surfactant molecule in the bulk of an "infinite" aggregate, and $-\alpha kT$ is the monomer-monomer interaction energy in the aggregate as opposed to the isolated monomer in solution. α is a constant which is characteristic of the interaction of surfactant monomers with each other and with the solvent, therefore we can assume that it has the same value for a given surfactant structure which will aggregate with both a prolate and an oblate geometry. For the same reason, μ_∞^0 is also invariant for both growth geometries for a given surfactant molecule. Figure 10 reports trends of $\mu_N^0{}_{prolate}$ and $\mu_N^0{}_{oblate}$ as a function of N (this approach is illustrated in Chapter 19 of Ref. [44]).

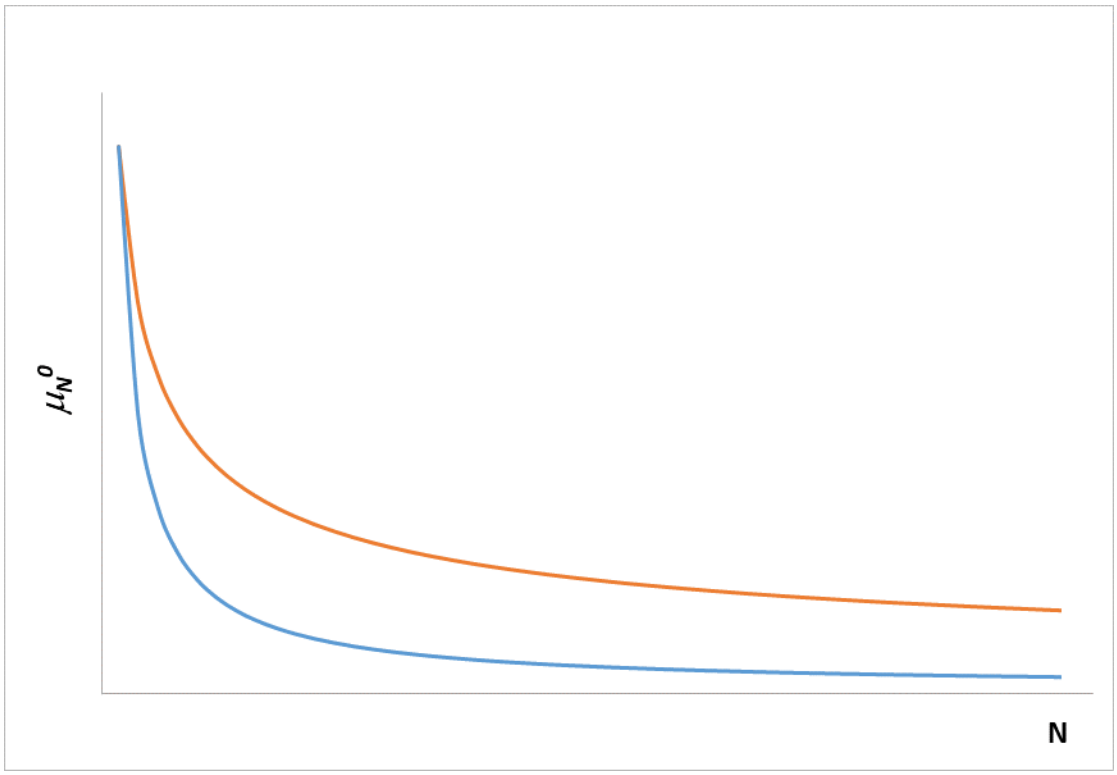


Figure 10. Trends of $\mu_N{}^0{}_{prolate}$ (blue) and $\mu_N{}^0{}_{oblate}$ (orange) as a function of N.

From Fig. 10, it is shown that micellar growth according to an oblate ellipsoid entails larger differences in free energies (and, consequently, chemical potentials) as N varies, as compared to a rod-like growth, thus possibly favouring a smaller polydispersity of aggregates. If we apply this finding to the low widths of size distributions observed with SBP3-14 and, particularly, with SBB3-14 at high NaOH concentrations, we may infer that micellar growth for those systems takes place according to a disc-like pattern. Perrin's relation relates the mean hydrodynamic radii of an oblate ellipsoid (e.g., a disc-like micelle), as determined by the Stokes-Einstein relation from DLS diffusion coefficients (equation 5), with the major and minor semi-axes a and b, respectively, of the ellipsoid:[47]

$$R_{h(Ob)} = \frac{b\left(\frac{a^2}{b^2}-1\right)^{\frac{1}{2}}}{\arctan\left(\frac{a^2}{b^2}-1\right)^{\frac{1}{2}}} \qquad (8)$$

On the basis that a micelle cannot have a hollow core, we may approximate *b* to the radius of "minimum sphere" of the micelle; therefore, *a* can be derived as the value satisfying the condition of $R_{h(Ob)} = R_h$. The following table shows calculations of *a* and *b* for sulfobetaine micelles in 1 M NaOH.

Table 3: Relation of measured hydrodynamic radii with the semi-axes of an oblate spheroid.

Sulfobetaine (M)	10^7 *D*, cm^2 s^{-1}	R_h, nm	*a*, nm	*b*, nm
SBE3-14 (0.2)	6.87	3.5	4.0	2.7
SBP3-14 (0.1)	7.81	3.1	3.4	2.6
SBB3-14 (0.15)[a]	4.71	5.2	6.5	2.8

[a] In 0.5 M NaOH.

3.3. $NaClO_4$

Diffusivity profiles of only SB3-14 + $NaClO_4$ are shown in Figure 11, whereas data relating to SBE3-14, SBP3-14 and SBB3-14 were not considered due to poor goodness-of-fit parameters (chi-squared, fit error, coefficients of variation; see Section *2.2*). At small concentrations of added perchlorate, diffusivity curves pass through a maximum at low surfactant concentrations; an increase in electrolyte results in a shift of these maxima towards higher sulfobetaine concentrations. For [$NaClO_4$] ≥0.2M, maxima disappear, and profiles enter a "phenomenological range" similar to that seen with NaBr, i.e., a monotonic increase of *D* with [SB3-14]. The sharp increases of diffusivity with [$NaClO_4$] = 0.005, 0.01 and 0.02 M indicate a strong charging of the micelles by perchlorate, which results in remarkable electrostatic repulsions, also enhanced by the modest contribution to the solution ionic strength by the electrolyte (free perchlorate concentration is relatively small). Zeta potential measurements show remarkably negative values for, e.g., 0.01 M SB3-14 in 0.005 M NaClO4 (ZP = -87.9 mW), which became less negative at 0.1 M SB3-14 (ZP = -41.5 mW). Transition of *D* through maxima may suggest that all available perchlorate is captured by the ammonium moieties of the micellar surface,

and increase in volume fraction (φ) with [SB3-14] leads to a dilution of the surface charge, with a consequent decrease in inter-micellar repulsions and a shift to a generally attractive interaction (remember that both terms of the first order disturbance at D_0 are directly proportional to φ; cf. eq. (1)) For high values of [$NaClO_4$], diffusivity curves tend to show an increasingly lower repulsive behaviour. This may be explained by considering that (i) under high ionic strength, repulsions will be effectively screened, and (ii) salt concentrations above that of surfactant in solution (i.e., for 0.5M $NaClO_4$), an entropically-driven invasion of both anions and cations into the interfacial micellar region, as already described,[3] may lead to a massive charge neutralization of micellar surfaces.

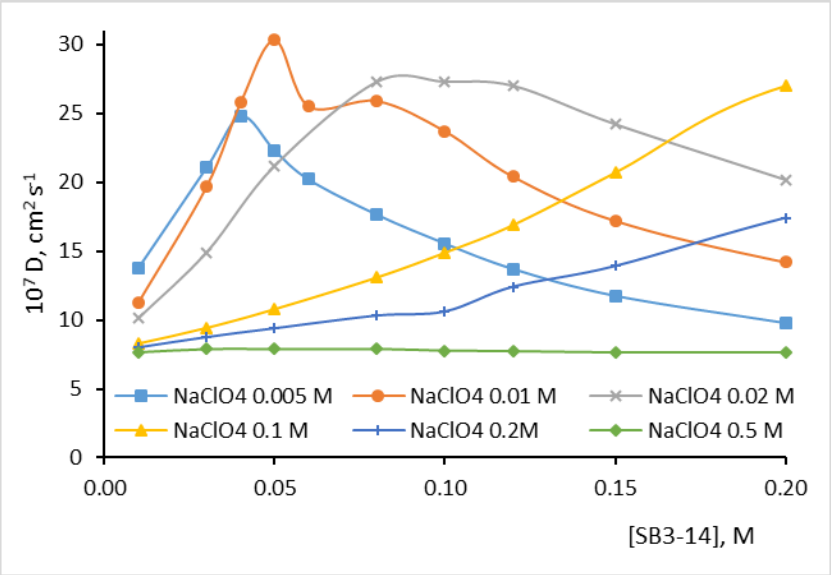


Figure 11. Diffusivity profiles for SB3-14 in water and different concentrations of $NaClO_4$ at 25.0°C.

Estimation of the hydrodynamic radii for SB3-14 micelles at the *cmc* in the presence of perchlorate is relatively straightforward, at least for curves at high (0.1-0.5 M) $NaClO_4$ concentration. Furthermore, those R_h values are close to R_h for SB3-14 in water, i.e., around 2.7 nm. On the other hand, some uncertainty arises when estimating extrapolated D values (and related R_h's) at low perchlorate concentrations, due to their high positive slopes. It should be kept in mind, though, that the significant increases in diffusivity observed at the lower perchlorate concentrations should not be attributed to a real "shrinkage" of the aggregates to approximately half the size of a minimum-sphere

micelle; rather, strong electrostatic repulsions should be considered as the main origin of such high diffusivities. Also, fluorescence quenching studies on SB3-14 micelles in water solution of perchlorate and other ions showed that *N* doesn't change detectably in the presence of interacting anions.[5] It should also be noted that increases in diffusivity values are accompanied by a significant increase in the coefficient of variation, CV (Table 5 in Supplementary Material). In our opinion, in an attempt to explain this finding, we should rule out any real effects on the size and shape of the aggregates, because with such "fast" diffusivity values we are approaching the resolving power of the DLS technique.

4. CONCLUSIONS

Sulfobetaine micelles show very peculiar properties, both in their mutual interactions, and as relates to their growth and shape. Diffusivity profiles of tetradecyl dialkylammonium propanesulfonate micelles in water (no added salts) show a slightly negative slope as the micellar volume fraction (or concentration) increases; this quasi-linear decrease of diffusivities is accompanied by a low coefficient of variation, indicating that micellar populations are essentially monodisperse. This finding is consistent with spherical, non-growing aggregates whose overall interaction potential is weakly attractive. Addition of salts with moderately "soft" anions such as bromides (i.e., NaBr) will negatively charge the micellar surface, leading to an increase of diffusion coefficients - and a general shift to positive slopes of *D* - with surfactant concentration. This behaviour does not seem to be greatly dependent on the bulk of the ammonium-linked alkyl moieties, as values of *D* reach approximately the same values at high surfactant concentrations for SB3-14 through SBB3-14. This finding seems partially at odds with reactivity data for model S_N2 reactions with bromide as the nucleophile at the surface of sulfobetaine micelles,[3] where it was shown that binding parameters for bromide ions to micellar surfaces decrease approximately by two-fold going from SB3-14 to SBB3-14. However, we should recall that diffusivity profiles are affected by both electrostatic

interactions *and* hydrodynamic perturbations, as reported in equation (1) as K_t and K_h, respectively; in particular, K_t and K_h affect D in opposite directions. A smaller number of micellar-bound bromide ions in SBB3-14 (i.e., less charged aggregates) will also be accompanied by a lower hydration of the micellar surface, as was also found through the analysis of chemical reactions of associated probes.[2] In turn, this may lead to different sensitivities of SB3-14 (more surface-hydrated) and SBB3-14 (less surface-hydrated) micelles to solvent (i.e., water) velocity fields, as accounted for by K_h in equation (3), resulting in a decrease of K_h for SBB3-14 as compared to SB3-14. This could explain the similar D values at high surfactant concentrations for the different sulfobetaines tested, against different values of surface charges.

Changing the anion to a less interacting one (i.e., NaOH), diffusivities sharply change as compared to NaBr, with slopes of D being invariably negative with all sulfobetaine and salt concentrations. A further difference is that a real micellar growth seems to be occurring, especially for SBP3-14 and SBB3-14 under high [NaOH]; this turns out to be particularly true with the latter sulfobetaine, as D curves no longer tend to a common intercept at the cmc. The sharp size monodispersity of micellar populations, together with geometrical and chemical potential considerations, led us to propose an oblate or disc-like growth pattern for those big-head sulfobetaine aggregates, even if this mere speculation should be confirmed by direct evidence.

On the other hand, when the added electrolyte has a strongly interacting anion, such as perchlorate, we observed for the first time an inversion of slope signs as SB3-14 concentration increases, at least for the lower $NaClO_4$ concentrations. This unprecedented behaviour of diffusivities has been ascribed to the strong binding of perchlorate anions to the ammonium moieties of the head groups, which massively charges up the micellar surface at low [surfactant], thus also contributing less to the solution ionic strength. As the surfactant concentration increases, ClO_4^- ions are increasingly adsorbed within the aggregates, up to the point where no more perchlorate is left to be bound, and the micellar surface charge starts to decrease. In turn, this leads to a decrease of electrostatic repulsions and, consequently, diffusivities. A strong interaction of perchlorate with sulfobetaines was previously

reported in the literature. For example, conductometry studies have shown that binding of ClO_4^- to SB3-14 is about ten-fold stronger than with Br^-, as also observed from ^{14}N line widths in NMR experiments.[3] Depletion of water at the micellar surface by ClO_4^- was also observed from reactivity studies,[6,38] even if this may appear in contrast with other findings showing that uptake of H_3O^+ in perchlorate-induced anionoid micelles.[5,39]

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Title:

Surface charge modulation of sulfobetaine micelles by interaction with different anions: A dynamic light scattering study

Authors:

P. Di Profio,* R. Germani, A. Fontana, V. Canale

SUPPLEMENTARY MATERIAL

Definition of goodness-of-fit parameters as reported in Section 2.2:

- Chi-squared is defined as a measure of the goodness of the fits relative to the data. It equals the square root of the sum of the squares of the differences between the autocorrelation channel data and the theoretical values obtained from the cumulans fit, divided by the estimated statistical fluctuation in the data points.
- Fit error is the normalized root-mean-square difference between the theoretical (fitted) autocorrelation function and the actual measured one, multiplied by 10,000. A Fit error of 1.0 represents an average difference between the fit and the raw data of 1 part in 10,000. It is a measure of the statistical noise on the autocorrelation function.

Dynamic Light Scattering Data

TABLE 1
Values of diffusivity (D) and coefficient of variation (v) for sulfobetaines SB(R)3-14 in water at 25°C.

1.1

[SB3-14], M	10^7 D, cm^2 s^{-1}	v, %
0.01	8.53	25.9
0.02	8.82	19.1
0.03	8.50	17.6
0.04	8.41	19.2
0.05	8.27	30.0
0.08	7.57	20.4
0.1	6.95	13.0
0.12	6.56	14.6
0.15	5.90	14.1
0.2	5.21	12.7

1.2

[SBE3-14], M	10^7 D, cm^2 s^{-1}	v, %
0.01	8.91	25.7

0.03	9.11	8.9
0.05	8.83	11.0
0.08	8.68	11.8
0.1	8.50	10.1
0.12	8.29	15.1
0.15	8.12	7.5
0.2	7.77	6.7

1.3

[SBP3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.36	18.1
0.03	9.21	11.1
0.05	9.20	12.4
0.08	9.05	12.8
0.1	9.00	11.9
0.12	8.92	10.7
0.15	8.82	12.9
0.2	8.61	13.2

1.4

[SBB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.96	20.6
0.03	10.05	18.3
0.05	9.78	21.3
0.08	8.97	15.5
0.1	8.77	20.3
0.12	8.47	19.8
0.15	7.98	19.9

TABLE 2

Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaines SB(R)3-14 in 0.02M NaBr at 25°C.

2.1

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.94	21.1
0.03	9.35	15.0
0.05	9.68	8.2
0.08	9.97	9.1
0.1	10.05	7.2
0.12	10.10	7.6
0.15	10.05	11.3
0.2	9.68	9.4

2.2

[SBE3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %

0.01	9.45	19.1
0.03	9.91	9.0
0.05	10.20	9.5
0.08	10.52	9.8
0.1	10.70	6.7
0.12	10.82	11.1
0.15	10.82	8.6
0.2	10.77	12.4

2.3

[SBP3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.63	36.9
0.03	8.63	13.4
0.05	9.96	13.7
0.08	10.40	13.0
0.1	10.80	10.6
0.12	11.02	8.7
0.15	11.22	11.0
0.2	11.30	14.9

2.4

[SBB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.04	22.2
0.03	9.32	11.5
0.05	9.30	10.9
0.08	9.28	11.7
0.1	9.16	8.7
0.12	9.06	12.5
0.15	8.71	11.8
0.2	8.23	13.6

TABLE 3

Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaines SB(R)3-14 in 0.1M NaBr at 25°C.

3.1

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.02	13.9
0.03	9.55	12.8
0.05	9.96	15.8
0.08	10.55	4.4
0.1	10.85	3.4
0.12	11.21	10.3
0.15	11.86	8.0
0.2	12.51	10.0

3.2

[SBE3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.48	42.6

0.03	9.40	18.6
0.05	10.25	15.9
0.08	10.93	16.8
0.1	11.33	10.4
0.12	11.83	13.6
0.15	12.44	13.1
0.2	13.15	12.3

3.3

[SBP3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.33	24.4
0.03	9.97	18.3
0.05	10.43	14.6
0.08	11.11	15.8
0.1	11.31	8.6
0.12	11.46	13.3
0.15	12.66	14.4
0.2	13.57	14.9

3.4

[SBB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.08	25.8
0.03	9.68	14.5
0.05	9.93	14.5
0.08	10.45	12.4
0.1	10.75	14.6
0.12	10.95	14.4
0.15	11.18	14.5
0.2	11.41	20.2

TABLE 4

Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaines SB(R)3-14 in 0.5M NaBr at 25°C.

4.1

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.99	24.2
0.03	9.13	17.3
0.05	9.62	7.6
0.08	9.95	12.5
0.1	10.31	10.1
0.12	10.57	7.6
0.15	11.03	14.0
0.2	11.75	10.7

4.2

[SBE3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.04	48.8
0.03	9.64	19.9
0.05	9.98	28.5

0.08	10.57	16.8
0.1	10.88	16.4
0.12	11.18	10.2
0.15	11.88	10.8
0.2	12.77	17.8

4.3

[SBP3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.25	25.6
0.03	9.67	13.8
0.05	10.00	18.2
0.08	10.54	17.5
0.1	10.98	20.1
0.12	11.29	22.6
0.15	11.70	16.4
0.2	12.72	19.8

4.4

[SBB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.34	15.8
0.03	9.65	12.2
0.05	10.01	13.9
0.08	10.47	14.4
0.1	10.82	12.8
0.12	11.18	17.2
0.15	11.65	7.4

TABLE 5

Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaine SB3-14 in various concentrations of $NaClO_4$ at25°C.

5.1 - $NaClO_4$ 0.005 M

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	13.80	32.9
0.03	21.10	54.9
0.04	24.80	48.4
0.05	22.30	47.3
0.06	20.20	42.4
0.08	17.65	44.6
0.1	15.55	40.7
0.12	13.70	42.3
0.15	11.75	40.9
0.2	9.77	36.2

5.2 - $NaClO_4$ 0.01 M

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	11.30	26.8
0.03	19.70	38.0
0.04	25.80	45.8
0.05	30.30	43.9

0.06	25.50	31.3
0.08	25.90	37.3
0.1	23.70	34.7
0.12	20.40	44.7
0.15	17.20	39.9
0.2	14.20	40.0
0.3	9.41	39.5
0.4	7.30	36.4

5.3 - $NaClO_4$ 0.02 M

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	10.10	9.4
0.03	14.90	27.7
0.05	21.20	39.4
0.08	27.30	47.9
0.1	27.30	50.6
0.12	27.00	45.1
0.15	24.20	46.5
0.2	20.15	44.9

5.4 - $NaClO_4$ 0.1 M

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.30	18.1
0.03	9.44	16.0
0.05	10.80	19.9
0.08	13.10	26.1
0.1	14.90	18.9
0.12	16.90	22.8
0.15	20.70	31.8
0.2	27.00	38.0
0.3	32.10	44.0
0.4	29.30	39.8

5.5 - $NaClO_4$ 0.2 M

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	7.99	16.8
0.03	8.74	18.5
0.05	9.38	17.8
0.08	10.30	16.4
0.1	10.60	33.7
0.12	12.40	22.2
0.15	13.90	25.6
0.2	17.40	24.4
0.3	23.60	45.6
0.4	26.60	58.2

5.6 - $NaClO_4$ 0.5 M

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	7.62	4.2

0.03	7.90	8.0
0.05	7.91	19.5
0.08	7.91	25.9
0.1	7.78	30.5
0.12	7.72	34.0
0.15	7.62	41.6
0.2	7.61	48.6

TABLE 6
Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaines SB(R)3-14 in 0.1M NaOH at 25°C.

6.1

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.74	25.9
0.03	8.67	15.1
0.05	8.38	9.6
0.08	7.78	5.3
0.1	7.42	6.3
0.12	7.08	9.1
0.15	6.55	11.7
0.2	5.91	5.3

6.2

[SBE3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.77	34.8
0.03	9.00	18.2
0.05	8.87	12.5
0.08	8.53	18.7
0.1	8.39	13.8
0.12	8.35	12.2
0.15	8.08	12.1
0.2	7.73	12.2

6.3

[SBP3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.09	7.8
0.02	9.17	15.1
0.03	9.23	15.9
0.04	9.16	5.8
0.05	9.01	14.4
0.06	8.91	20.9
0.08	8.72	24.0
0.10	8.88	9.3
0.12	8.79	7.6
0.15	8.65	8.2
0.20	8.55	14.9

6.4

[SBB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.79	18.4
0.02	8.74	16.0
0.03	8.69	14.2
0.04	8.50	7.3
0.05	8.39	8.4
0.06	8.25	10.4
0.08	7.89	16.5
0.10	7.69	10.1
0.12	7.40	4.4
0.15	7.12	9.5

TABLE 7

Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaines SB(R)3-14 in 0.5 M NaOH at 25°C.

7.1

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.99	20.0
0.03	8.65	12.5
0.05	8.28	12.5
0.08	7.75	19.1
0.1	7.50	8.9
0.12	7.27	12.7
0.15	6.73	8.4
0.2	6.08	11.1

7.2

[SBE3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.91	29.5
0.03	8.82	24.0
0.05	8.72	18.7
0.08	8.40	19.3
0.1	8.18	18.1
0.12	8.13	16.2
0.15	7.59	22.6
0.2	7.47	14.9

7.3

[SBP3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.06	22.0
0.02	9.16	13.4
0.03	9.09	12.9
0.04	9.06	2.6
0.05	8.97	6.8
0.06	8.91	8.0

0.08	8.77	5.7
0.10	8.56	10.1
0.12	8.42	6.9
0.15	8.19	6.3
0.20	7.87	6.9

7.4

[SBB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	8.70	19.3
0.02	8.29	7.8
0.03	8.05	12.4
0.04	7.55	4.8
0.05	7.29	8.0
0.06	6.99	9.7
0.08	6.36	8.7
0.10	5.83	11.1
0.12	6.02	7.8
0.15	4.71	7.1

TABLE 8

Values of diffusivity (*D*) and coefficient of variation (*v*) for sulfobetaines SB(R)3-14 in 1.0 M NaOH at 25°C.

8.1

[SB3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.06	27.2
0.03	8.66	15.8
0.05	8.25	11.6
0.08	7.64	7.0
0.1	7.25	11.9
0.12	6.94	12.9
0.15	6.45	10.1
0.2	5.71	11.6

8.2

[SBE3-14], M	10^7 *D*, cm^2 s^{-1}	*v*, %
0.01	9.16	25.3
0.03	8.98	16.7
0.05	8.68	14.0
0.1	8.15	14.2
0.15	7.54	13.4
0.20	6.87	10.1

8.3

[SBP3-14], M	10^7 D, cm^2 s^{-1}	*v*, %
0.01	9.30	14.3
0.02	9.11	7.3
0.03	8.92	10.8

0.04	8.72	8.5
0.05	8.60	7.5
0.06	8.48	7.1
0.08	8.10	3.3
0.10	7.81	9.4