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Counteranion Effect on Micellization of Cationic Gemini Surfactants 14-2-14: Hofmeister and Other Counterions

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The effect of counterions was investigated and analyzed to probe the principal ionic effects influencing the micellization behavior of dimeric cationic surfactant ethanediylbis(dimethyltetradecylammonium), referred to as gemini 14-2-14. The 30 counterions were classified to four different families depending on their nature: (1) small and inorganic counterions which are typically taken from the Hofmeister series were studied to focus on the effect of ion type; (2) *n*-alkyl carboxylate counterions were studied to focus on the effect of the hydrophobicity of counterions; (3) aromatic carboxylate counterions were included to focus on the effect of the position of substitutions; and (4) other counterions were included in order to shed light on other parameters. By investigating the critical micelle concentration (CMC), ionization degree of micelle (α), free energy of micellization (ΔG_M), and aggregation numbers *N* of the gemini surfactant with these different types of anions, we demonstrated the effect of different ion properties independently. This approach allowed us to describe the effect of counterions on the micellization behavior of the gemini surfactant in terms of complex interplay between hydrophobicity of anions and other ion properties such as counterion hydration, interfacial packing of ions, and ionic morphology. Indeed, our results clearly demonstrate that a counterion effect on micellization properties cannot be described as a result of one single parameter of ions, as is too often assumed, but rather the balancing effects cooperatively affect the propensity of counterions to form ion pairs with surfactant headgroups and the entropy gain upon micellization. These results provide new insight in understanding the effect of ions on the delicate balance of forces controlling aggregate morphology and solution properties of charged amphiphilic molecules.

Introduction

Salt effects on protein solutions has been widely reviewed since the nineteenth century with the works of Hofmeister.^{1,2} However, classical theories based on van der Waals interactions and electrical double layer still fail to explain a basic fundamental observation: The relative efficiency of ions to precipitate proteins is always the same, irrespective of the protein system. For this reason, semiempirical parameters such as the lyotropic number have been used in order to rationalize the Hofmeister effects. For example, Collins and Washabaugh³ proposed a model in which the degree of organization of water molecules surrounding the ion is crucial. In this model, kosmotropic ions, also called structure-makers, are described as ions which exhibit strong interactions with water, whereas chaotropic ions, or structure-breakers, are those ions that are less hydrated and thus less effective in organizing surrounding water molecules. In a phenomenological approach, many attempts to correlate Hofmeister effects with other properties of ions have been proposed.⁴ Thermodynamical properties of ions, free energy and entropy of hydration, free

energy of transfer from aqueous to organic phase, hydrated ionic radii, Jones–Dole viscosity B-coefficients, surface tension increment, partial molar volume, and polarizability closely correlate with the Hofmeister hierarchy of ions. Recently, Ninham and Yaminsky have highlighted the importance of the dispersion forces, which are not included in classical DLVO theories, in determining the Hofmeister series, which they related to the polarizability of the ions.⁵ Taking into account these forces allowed them to model the ionic effects more precisely.

It would be impossible to draw up the exhaustive list of phenomena affected by ionic effects.⁶ In biological systems for instance, the water absorbance of wool fibers or the growing of a bacterium are related to ion specificity.⁷ A number of reports have dwelled on the ion dependence of the surface tension of aqueous electrolyte solution by molecular simulation study.⁸ Bubble interactions and coalescence are also known to be influenced by salt effects.⁹ Surfactants at the air–water interface

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exhibit selective binding to ions when spread on electrolyte solutions.¹⁰ The ion specificity can also be observed by the adsorption of ions at a simple aqueous interface of ionic solution.¹¹ More generally, ionic amphiphile behavior in solution is strongly influenced by the background salt, and this effect can be observed by monitoring the variation of the critical micellar concentration (CMC),¹² Krafft temperature, ionization degree, aggregation number,¹³ the amount of water or the counterions in the interfacial region as measured by “chemical trapping” measurements,¹⁴ or the morphology and dynamics of self-assembly,^{15–17} in particular micellization, morphological transitions, and growth of micelles^{18,19} upon the addition of electrolytes. While these numerous studies clearly indicated the importance of ionic parameters such as ion size, polarizability, or hydrophilicity; it was also noted that the properties of the aggregates such as cmc or micellar growth do not depend solely on one single parameter. Also, while the effect of added salt to cationic surfactant solutions has been widely investigated, there are relatively few reports on the *direct* effect of counterions of ionic surfactants in the absence of salt.^{20–22} Changing the counterion of a surfactant mainly affects their affinity with the ionic aggregates surface.

The properties of ionic surfactants possessing small counterions such as halides generally show a correlation with the Hofmeister series, known to be related to the polarizability of ions. It is generally proposed that in water, hydrophobic/chaotropic

counterions are bound more strongly to the micellar surface than hydrophilic/kosmotropic counterions. Chaotropic anions are also more effective in promoting the micellar growth of ionic surfactants than kosmotropic ions.¹⁴ Thus, an increase of the hydrophilicity (hydrated ionic radius) or a decrease of the hydrophobicity (polarizability) of the counterions generally reduces its affinity toward ionic micellar surfaces and the tendency to form ion pairs, leading to higher ionization degrees. This penalizes the micellization process and leads to higher values of CMC. It is often reported that the hydrophobic effect and the chain length have a stronger effect on CMC than the counterion nature which influences the electrostatic interaction between the polar heads.^{19f}

In the case of polyatomic ions, the effect of ion properties on the aggregation behaviors of the amphiphiles can be largely perturbed by steric effects or inter/intra molecular interactions. The studies on micellization of surfactants such as alkyltrimethylammonium,^{23,24} dialkyldimethylammonium,²⁵ gemini surfactants 12-6-12,^{22a} 1-methyl-4-*n*-dodecylpyridinium,²⁶ cationic bolaamphiphile (1,1'-(1,ω-tetradecanediy)bispyridinium), or alkylpyridinium^{27,28} in terms of the effects of counterion were reported with various anions such as halides or alkylsulfonates, as well as benzoate derivatives. In these cases, the dependence of their CMC and ionization degree of the micelles cannot clearly be described as a function of a single known parameter, or the nature of counterion (ion size, polarizability, or ion hydrophilicity). For example, in the case of aromatic anions, the position of substituents enhances or hinders micellar stability due to steric effects.

Gemini surfactants are a group of amphiphilic molecules which have more than two or more identical or different amphiphilic moieties connected by a spacer group.²⁹ These surfactants have generated much interest over the past 20 years owing to their particular aggregation behavior as well as enhanced surface activities.^{30–33} Despite the structural diversity of gemini in the literature, only a few studies have focused on the counteranion effect on the properties of bisquaternary ammonium-type cationic gemini surfactants *n-s-n* with counterions other than bromide or chloride. Other than our own studies involving chiral anions such as tartrate, malate, glucarate, gluconate,^{34a–c} as well as peptides^{34d} or nucleotides^{34e,34f} counterions, the work of Jiang et al.^{22a} shows results comparing the effect of several counterions on micellization of *n-s-n* gemini surfactants.

Herein we report our study of 14-2-14 gemini surfactants paired to 30 different counterions (Chart 1) classified into four

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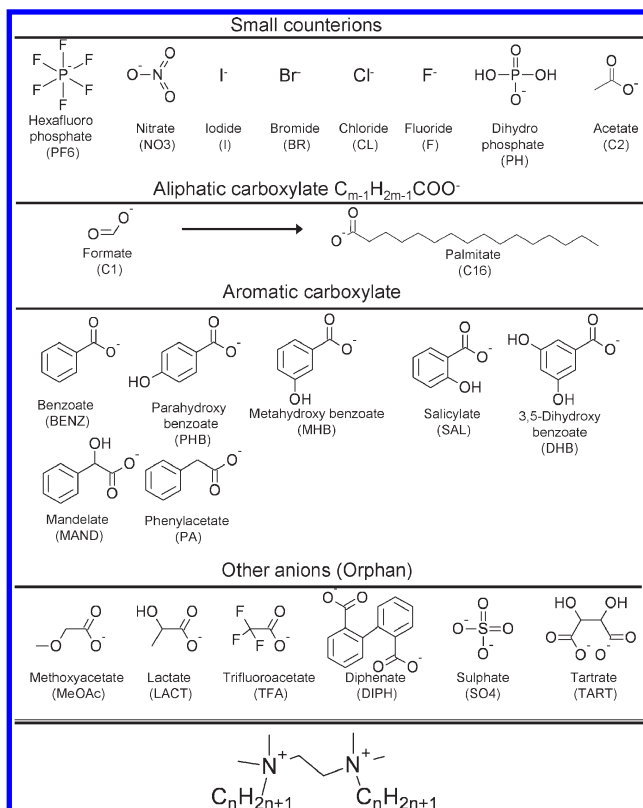
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Chart 1. Cationic Gemini Surfactant n -2- n with X^- Counterion, Denoted as n -2- n X or n X

principal groups: (1) small counterions, which are principally ions taken from the Hofmeister series, (2) aliphatic carboxylate counterions, in which the hydrophobicity of the anion can be tailored by modifying the alkyl group, while keeping the same ionic nature, (3) aromatic carboxylate counterions with which the effect of substitutions can be examined, and (4) those which do not belong to the first three families but which allow comparisons based on particular properties (“orphan” counterions). The micellization of these amphiphile molecules (CMC, ionization degree, α , aggregation number) have been investigated using conductivity and fluorescence measurements. We focused on gemini surfactants in light of their specific properties, such as their high solubility and significantly lower CMC values compared to their single chain analogues. Also, as demonstrated by us previously, the use of gemini surfactant gives access to a much richer morphological variety of aggregates.^{35,36}

The results globally confirm the tendencies expected from the hydrophobicity/hilicity of anions which promotes/inhibits micellization. However, for small or aliphatic anions, the additional entropic effects associated with the liberation of water molecules during micellization are clearly observed. Steric effects and inter/intra molecular interaction *via* hydrogen bonding are also important as observed from aliphatic and aromatic carboxylate anions. Our observation also demonstrate unambiguously that no single ion property (ion size, hydrophilicity, polarizability, pK_a , ion morphology, etc.) correlates with micellar property such as CMC and α but the ensemble of these parameters determines their propensity to form ion pairs with surfactant head groups and the entropy gain associated with micelle formation, which controls the formation of micelles and micellar properties.

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For all the investigated systems, the aggregation numbers of the micelles fall within a very narrow range as a function of normalized concentration D_t/CMC , systematically increasing regardless of the counterions and ionization degrees. This indicates that the number of micelles depends very little on the nature of the counterion but only on the total surfactant concentration, suggesting that the concentration of micelles is determined principally by entropy.

Experimental Section

Sample Preparation. Gemini surfactants were synthesized as described previously.³⁵ Counterions were exchanged to those shown in Chart 1. For ion-exchange methods, see Supporting Information.³⁴

Conductivity Measurements. Values were obtained with a Consort C830 (Belgium) conductimeter equipped with a platinum electrode SK10T (cell constant 1.0 cm^{-1}). The conductivity was measured in a temperature-controlled double-walled glass container with a circulation of water and was determined to within $0.1\text{ }\mu\text{S}$ for conductivity lower than $100\text{ }\mu\text{S}$, and to within $1\text{ }\mu\text{S}$ for larger values. The temperature was controlled to within $0.1\text{ }^\circ\text{C}$ for all experiments.

CMC. The CMC measurements were performed at 30 and $60\text{ }^\circ\text{C}$ for gemini with a high Krafft temperature. A stock solution of surfactant in ultrapure water was successively added to a known volume of ultrapure water. The conductivity κ versus surfactant concentration C was plotted, and the CMC was obtained from the concentration, which corresponds to the intersection of the conductivity κ extrapolated from the experimental values below ($S_1 = \kappa_{C < CMC}$) and beyond the CMC ($S_2 = \kappa_{C > CMC}$). However, the change of slope is not always very clear, so the first (or second) derivative^{37–39} is also analyzed. In this work, we determined the CMC by tracing the first derivative dk/dC starting from the experimental values of $\kappa = f(C)$, and by applying regression of a logistic type $f(x) = (A_1 - A_2)/(1 + (x/x_0)^{p-A_2})$ using the software OriginPro 7.5. The CMC corresponds to the inflection point of the logistic function x_0 , and the parameters A_1 and A_2 correspond respectively to the slopes S_1 and S_2 . The parameter p characterizes the width of concentration range where the transition takes place: the higher the value of p , the more the transition occurs over a narrow concentration range.

Ionization Degree α . The ionization degree α , that is, the fraction of charges of free counterions, has been determined by two different methods. By far the most common approach is to use the ratio of the slopes of the conductivity beyond and below the CMC where $\alpha_a = S_2/S_1$ even though it has been shown⁴⁰ that this method yields overestimated α values. In the alternative method, for an ionic surfactant made of i polar heads (charge z_s) and a counterion (charge z_c), Evans has evaluated that α is related to the number of aggregation N by the following equation:⁴¹

$$S_2 = \alpha_b^2 N^{2/3} (S_1 - \Omega \lambda_X) + \alpha_b \Omega \lambda_X \quad (1)$$

where λ_X ⁴² is the ionic molar conductivity at infinite dilution of the counterion and Ω is a parameter which depends on the

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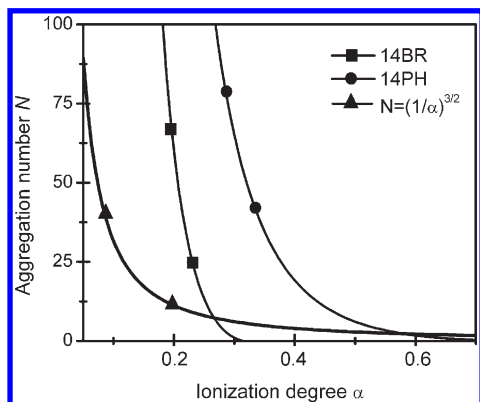


Figure 1. Examples of curves for aggregation number N as a function of the ionization degree α_b using eq 2 for 14BR (■) and 14PH (●). The curve ▲ represents eq 3.

number of polar heads per surfactant molecule i , the charge of each polar head z_s , and the charge of the counterion z_c : $\Omega = |iz_s|z_c$. This requires that the N be determined independently. The ionization degree α_b is significantly lower than α_a , but the tendencies observed remain similar.²⁹ When λ_X is known, it is possible to trace the evolution of the number of aggregation N according to the ionization level α_b of micelles of surfactant given by rewriting eq 1:

$$N = \left(\frac{S_2 - \alpha_b \Omega \lambda_X}{\alpha_b^2 (S_1 - \Omega \lambda_X)} \right)^{3/2} \quad (2)$$

Figure 1 presents two examples (14BR and 14PH) of $N = f(\alpha_b)$ curves obtained from experimental results. First, it is observed that a slight variation of the ionization degree α_b results in a large deviation of aggregation N . Moreover, if the number of aggregation can vary theoretically *ad infinitum*, the ionization degree can vary only in a relatively restricted range for a given amphiphile, and this range is larger for the molecules with higher ionization degrees. For example, 14BR forms only partly ionized micelles with α_b varying between 0.18 and 0.23 for $N > 20$, whereas the α_b of highly ionized 14PH micelles vary from 0.25 to 0.4 for the same range of aggregation sizes considered. The difference²⁹ between the ionization degrees obtained from two models (α_a and α_b) mainly originates from the approximation used for the calculation of the molar conductivity of an ionic micelle λ_M . α_a ⁴³ uses the approximation that surfactants in micelles whose charge is not neutralized by bound counterions contribute to the conductivity of the solution as equally as those of free molecules, $\lambda_M = N\alpha\lambda_A$, whereas α_b is calculated with a higher estimated micellar ionic conductivity, $\lambda_M = N^{5/3}\alpha^2\lambda_A$.⁴¹ When the two expressions of λ_M are equal, one obtains $N\alpha\lambda_A = N^{5/3}\alpha^2\lambda$ which leads to

$$N = \left(\frac{1}{\alpha} \right)^{3/2} \quad (3)$$

The curve described by eq 3 represents the point of agreement between the two models (Figure 1), and its points of intersection with $N = f(\alpha_b)$ thus have as an x -coordinate the ionization degrees α_a for the same systems. As it is shown in the figure, for most of the systems the corresponding N values obtained from the intersection of eqs 1 and 3 are unrealistically small ($N \lesssim 10$) and largely overestimate values of α_a .

In this study, we use both ionization degrees α_a and α_b for aggregation number N denoted as $\alpha_{b,N}$ hereafter, when the ionic molar conductivity of the counterion is available in the literature. As it will be discussed later, the N of the micelles determined with fluorescence measurements just above the CMC shown (see

Table 1. CMC, α_a , $\alpha_{b,25}$, $\Delta G_{M,25}$ of 14-2-14 with Small Counterions at 30 °C unless Indicated Otherwise

gemini	CMC (mM)	ionization degree α_a	ionization degree $\alpha_{b,25}$	$\Delta G_{M,25}$ (kJ·mol ⁻¹)
14BR	0.14	0.27	0.23	-27.05
14NO ₃	0.14	0.25	0.23	-27.09
14CL	0.26	0.29	0.26	-24.39
14C ₂	0.61	0.48	0.33	-20.65
14F	0.64	0.55	0.33	-20.58
14PH	1.23	0.58	0.38	-17.87
14I	0.10 (60 °C)	0.49		

below) is ~ 25 and regardless of the counterions for a given concentration up to $2.0 \times \text{CMC}$.

Aggregation Numbers N Determined by Spectrofluorometric Measurements. The aggregation numbers N were determined using a spectrofluorometric technique.⁴⁴ Micelle concentrations (number of micelles per unit volume) [Mic] were determined according to

$$\ln \frac{I}{I_0} = - \frac{[Q]}{[\text{Mic}]} \quad (4)$$

where I and I_0 represent fluorescence intensities at λ_{max} in the presence and in the absence of quencher, respectively, $[Q]$ is quencher concentration, and $[\text{Mic}]$ is the concentration of the micelles. Values of N were determined as $N = [D]/[\text{Mic}]$, where $D = D_t - \text{CMC}$, D_t is total surfactant concentration and D is concentration of micellized surfactant. The typical fluorescence spectra and dependence $\ln(I/I_0)$ versus quencher concentration for different D_t is available in the Supporting Information (Figures S.1 and S.2). In the case of 14Ac (C₂), N was also determined by time-resolved fluorescence quenching (TRFQ) using 1-methylpyrene as the probe and 2,3-dimethylbenzophenone as the quencher.⁴⁵ (see Supporting Information).

Free Energy of Micellization $\Delta G_{M,N}$. The free energy of micellization $\Delta G_{M,N}$ for the formation of micelles with N surfactant molecules and the ionization degree $\alpha_{b,N}$ is calculated by the equation⁴⁶

$$\Delta G_{M,N}^\circ = RT \left(\frac{1}{j} + \beta \frac{\Omega}{j} \right) \ln \text{cmc} + RT \left(\beta \frac{\Omega}{j} \ln \frac{\Omega}{j} - \frac{\ln j}{j} \right) \quad (5)$$

In eq 5, j is the number of apolar chains per surfactant molecule, cmc is the critical micellar concentration in mol of alkyl chain per liter, β is the fraction of charges of micellized surfactants ions neutralized by micelle-bound counterion ($\beta = 1 - \alpha_{b,N}$). In this manuscript, CMC is used for the critical micellar concentration in mol of gemini surfactant per liter, that is, for two-chain gemini, $2\text{CMC} = \text{cmc}$.

Results

Small Counterions. The CMCs of the 14-2-14 gemini paired to small counterions are shown in Table 1. As expected, the CMC of the gemini 14-2-14X evolved according to the Hofmeister series: I < NO₃ \sim BR < CL < F \sim C₂ < PH. We should note that the CMC of 14I was measured at 60 °C due to its low solubility. As the CMC tends to increase with temperature, the reported value is probably overestimated. As for 14F, we encountered stability problems (further detailed in the Supporting Information), and its CMC value should be taken with caution.

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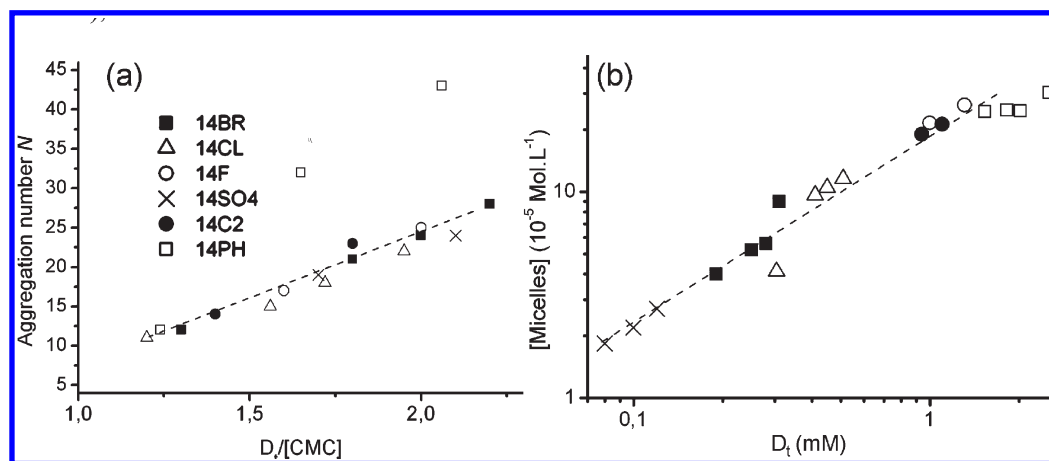


Figure 2. (a) Aggregation numbers and (b) micelle concentration $[Mic]$ plotted as a function of ratio D_t/CMC and total surfactant concentration D_t , respectively, for micelles of 14-2-14 with small counterions: (×) 14SO₄, (■) 14BR, (Δ) 14CL, (●) 14C₂, (○) 14F and (□) 14PH.

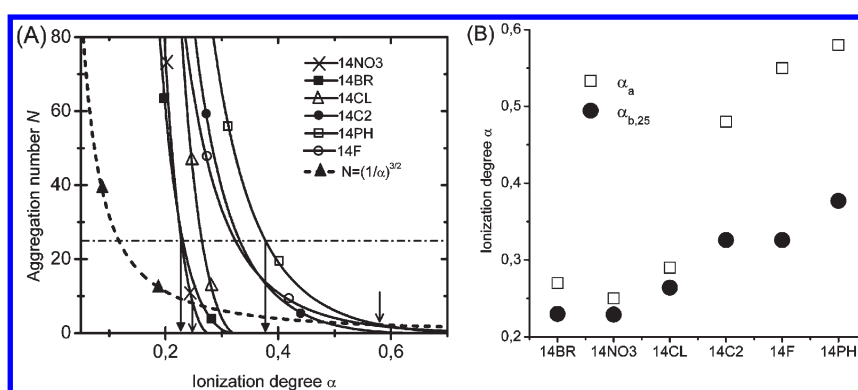


Figure 3. (A) Aggregation numbers as a function of the ionization degree α . Intersection with $N = 25$ gives $\alpha_{b,25}$, and intersection with $N = (1/\alpha)^{3/2}$ gives α_a (examples are shown for 14NO₃ (filled arrows) and 14PH (open arrows)). (B) α_a and $\alpha_{b,25}$ for the 14-2-14 with small counterions (measured at 30 °C).

The N values and concentration of micelles $[Mic]$ obtained from fluorescence quenching measurements are represented versus normalized concentration with CMC, D_t/CMC , and the surfactant concentration D_t in Figure 2 in the range of concentration just above the CMC up to twice the CMC. Interestingly, the aggregation numbers fall on a single line when they are plotted as a function of D_t/CMC , regardless the nature of the anion, Figure 2a.⁴⁷ They are ~ 10 for all the 14-2-14 of this series, and reach about 25 for the concentration about twice the CMC. Beyond this concentration, the aggregation number for some of the gemini showed accelerated increase deviating from linear dependency which indicates that micelles start to elongate beyond $D_t/CMC = 2$.^{14d,f} Meanwhile, the concentrations of micelles $[Mic]$ are insensitive to counterion type when plotted as a function of D_t (Figure 2b). Here, it is important to note that gemini have two hydrocarbon tails, which explains the smaller values (about one-half) of N compared to classic monomeric surfactants.⁴⁸

To confirm the aggregation numbers obtained from static fluorescence quenching,⁴⁹ we used dynamic light scattering (DLS) and TRFQ measurements to determine the aggregation number of 14-2-14Ac (C₂) at 2CMC. Both techniques gave values which are very close to the value obtained from static quenching ($N = 25$): from light scattering measurements, a value

of $N = 22 \pm 3$ was obtained, whereas the N value determined from TRFQ was 26 ± 4 . In the rest of the manuscript, the values of the ionization degree and the micellization free energy were calculated using a fixed number $N = 25$ at a fixed concentration 2CMC.

Figure 3A presents the curves relating the aggregation numbers N and ionization degrees α_b for each counterion as determined from conductivity measurements at 30 °C. Using $N = 25$, we can obtain $\alpha_{b,25}$, whereas the intersections of each curve with $N = (1/\alpha)^{3/2}$ give the values for α_a . The two values are compared in Figure 3B where we clearly remark that they both follow the same trend which agrees with the Hofmeister series and increases with the hydrophilicity of the anions. As expected, the values of $\alpha_{b,25}$ are globally smaller than α_a .

Table 1 gathers the CMC, the ionization degrees and the free energies of micelle formation with 25 gemini molecules $\Delta G_{M,25}$ with small anions at 30 °C obtained from the eq 5.

The micellization free energy (Table 1) ranges from $-17.87 \text{ kJ}\cdot\text{mol}^{-1}$ for the least favorable micellization with kosmotropic ions (14PH) to $-27.17 \text{ kJ}\cdot\text{mol}^{-1}$ for the most favorable micellization with chaotropic ions (14BR) following the order: BR \approx NO₃ < CL < C₂ < F < PH. The same order was observed for the evolution of the CMC values as well as ionization degree: higher $\Delta G_{M,25}$ correlates with higher CMC and ionization degree with the presence of more ionized micelles and the micellization process is less endothermic compared to gemini with chaotropic counterions. In general, the values obtained for 14BR and 14NO₃ are very close. The ionization degree α_b of 14PH reached 0.38,

(47) Except for 14PH which shows higher aggregation numbers.

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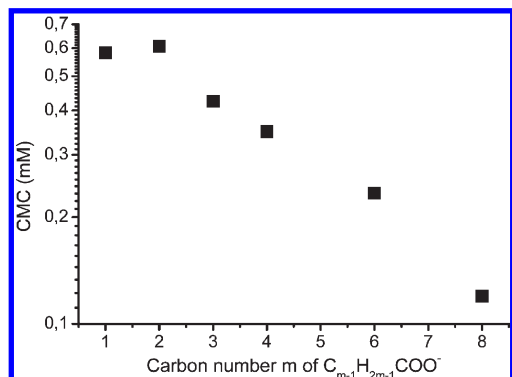


Figure 4. CMC of the 14-2-14 with aliphatic carboxylate counterions $C_{m-1}H_{2m-1}COO^{-}$ at 30 °C.

whereas the α_b of 14BR is 0.23, close to the values observed for bromides of alkyltrimethylammonium (ca. 0.2).²⁹ The free energy of micellization $\Delta G_{M,25}$ of 14BR is also similar to the value expected from published results.⁴⁶

Aliphatic, Aromatic, and Orphan Carboxylate Counterions. *Aliphatic Carboxylate Counterions.* The aliphatic carboxylate counterions highlight the effect of hydrophobicity variation of the counterions. Figure 4 shows the CMC of the gemini 14-2-14 with aliphatic carboxylate counterions as a function of their chain length. The CMC decreases monotonously with increasing chain length, except for a maximum at $m = 2$. As it will be shown later, the aggregation numbers N of the gemini with aliphatic carboxylate counterions show the same evolution as was observed with small anions: N increases indifferently with m as a function of D_t/CMC , between $N \approx 10$ (at $D_t/CMC = 1$) and $N \approx 25$ (at $D_t/CMC = 2$). Therefore, α_b was evaluated for $N = 25$ as it is shown in Figure 5A, and the curves of α versus chain length are presented in Figure 5B.

Interestingly, the ionization degrees of the aliphatic carboxylate family of surfactants evolved through a maximum, following the order $C3 \approx C4 > C2 > C1 > C6 > C8$ instead of decreasing monotonously as intuitively expected. The two ionization degrees α_a and $\alpha_{b,25}$ have similar trends again. It is interesting to note that the ionization degrees $\alpha_{b,25}$ of this family, except for 14C8, are all between 0.29 and 0.38, higher than the values of 14BR (0.23) and 14CL (0.26) in spite of the presence of hydrophobic chains.

The free energies of micelle formation (in $\text{kJ} \cdot \text{mol}^{-1}$) with 25 surfactant molecules $\Delta G_{M,25}$ for gemini 14-2-14 and their evolution with the length of alkyl chain of counterion, as calculated from eq 5 and $\Omega = 2$, Figure 6, allows us to directly evaluate the influence of the alkyl chain length of the counterion on the micellization process. The general evolution of the free energy of micelle formation indicates that micellization is favored as the length of hydrophobic chains of the counterion increases. The least negative value for $m = 2$ agrees with observations deduced from the CMC.

Aromatic Carboxylates Counterions. Because of the low solubility of most of the gemini surfactants with aromatic carboxylate counterions presented in Chart 1 (Krafft temperature higher than 60 °C at 3 mM, except for 14PA and 14MAND), we could not determine N_{aggr} from fluorescence measurements. Thus, it was not possible to estimate the micellar concentration [Mic] and α_b , and so, for this family of counterions, we only compare the CMC values and α_a as shown in Table 3 (more detail in the Supporting Information).

The values of the CMCs evolve following the order $SAL < BENZ < MHB < PA < MAND < PHB < DHB$. This order agrees with what was reported by Bijma and Engberts in the study

using 1-methyl-4-*n*-dodecylpyridinium,²⁶ except for PA, MAND, and DHB not included in their study. While the CMC showed an important difference between different counterions, the ionization degrees were practically the same (~ 0.45) except for 14SAL which had a very low ionization degree (0.14). This is probably due to the strong hydrophobicity of SAL ions as it will be discussed later.

Orphan Counterions. These counterions are selected to highlight the impact of key modifications of the chemical structure of the counterion on the micellization of the gemini surfactant. Table 3 presents the results obtained with orphan counterions PA and MAND at 30 °C and with aromatic carboxylate counterions at 60 °C.

Aggregation Number N , and Micelle Concentration [Mic] of 14-2-14 with Aliphatic, Aromatic, and Orphan Carboxylate Counterions. The N and [Mic] of 14-2-14 with counterions alkylcarboxylate $C_{m-1}H_{2m-1}COO^{-}$ for $m = 1, 2, 3, 6$, and 8, TFA, PA, and MeOAc are presented in Figure 7.

These results confirm the observations gleaned using small counterions: The aggregation number of each surfactant increases as a function of the ratio D_t/CMC and is independent of the nature of the counterion as long as the micelles are spherical. Micelle concentration, on the other hand, depends mainly on the D_t for concentrations close to the CMC.

Discussion

We will now take closer look at the correlation between the ionic parameters and the observed micellar properties such as CMCs, α , and N values of micelles. It becomes obvious that the hydrophobicity of ions is an important parameter but cannot alone account for the variation of these micellar properties.

Anion Properties and Hofmeister Effects: Small Anions. The physical properties of the anions studied are presented in Table 4, arranged in the order usually observed in the Hofmeister series, that is, by decreasing lyotropic number N , from the more chaotropic ions (top) toward more kosmotropic ions (bottom). The iodide ion is the largest in the halide ion series, the most polarizable ($\alpha = 7.51$), the most acidic ($\text{p}K_a = -11$), and also the least hydrated ($n_H = 1.6$). Its energy of transfer ΔG_{HB} is largely negative, showing that it is a very chaotropic anion which destroys the structure of water in its vicinity. At the opposite end of the halide series, the fluoride ion displays properties radically opposite since it is the smallest anion, the least polarizable ($\alpha = 0.88$), the most hydrated ($n_H = 2.8$), and the most kosmotropic ($\Delta G_{HB} = 0.08$). It is also the least acidic ($\text{p}K_a = 3.17$) among the halogenous acids. The two other halides Br^{-} and Cl^{-} have intermediate properties and all the parameters presented at Table 3 evolve systematically in the order I, BR, CL, and F.

While the behavior of halide ions follows the expected trend, the variation of the parameters for other polyatomic anions such as NO_3 , C_2 and PH is not systematic. Among the parameters listed, only two of them are more or less proportional to the lyotropic number N : the free energy of hydration ΔG_{hyd} , and the change in the average number of hydrogen bonds per water molecule resulting from the presence of the ion (ΔG_{HB}).⁵¹ The three other parameters, that is, partial molar volume v_s , polarizability α , and number of hydration n_H do not follow the systematic trend with the hydrophobicity of ions for the polyatomic anions. NO_3 has much higher $\text{p}K_a$, relatively high n_H , and

(50) For C8, theoretical value extrapolated from experimental S1 of C4 and C6 was used.

(51) Yizhak, M. *Ion Properties*; Marcel Dekker Inc.: New York, 1997.

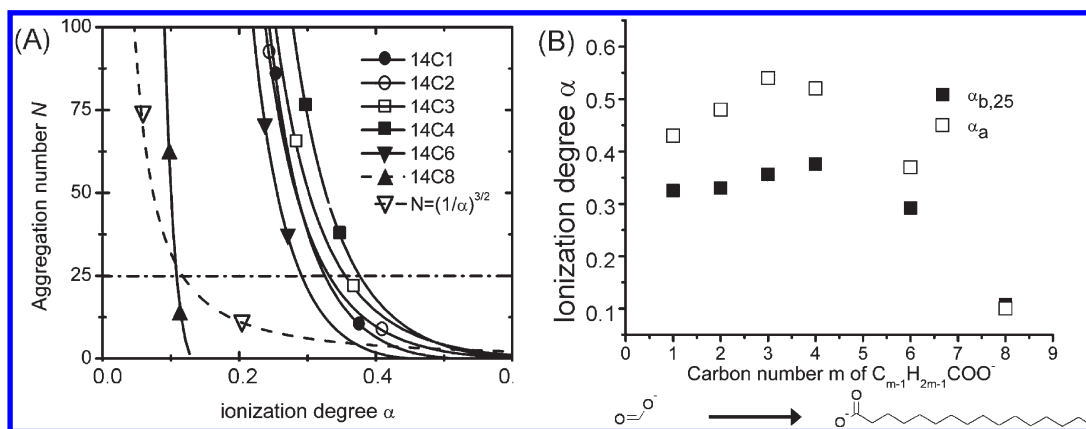


Figure 5. (A) Aggregation number N as a function of the ionization degree α for gemini 14-2-14 with aliphatic carboxylate counterions. Intersection with $N = 25$ gives $\alpha_{b,25}$ and intersection with $N = (1/\alpha)^{3/2}$ gives α_a . (B) α_a and $\alpha_{b,25}$ for gemini 14-2-14 with alkyl carboxylate counterion with different length.⁵⁰

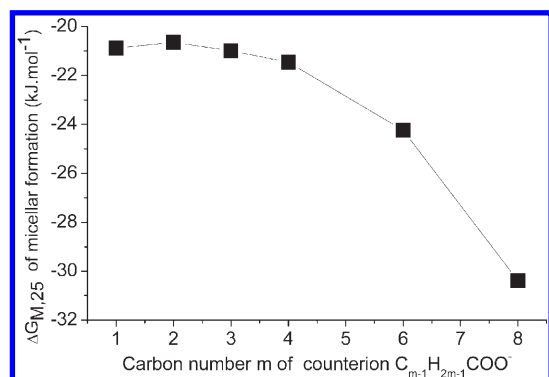


Figure 6. Dependency of the free energies of micelle formation ($N = 25$) $\Delta G_{M,25}$ with the chain length of the aliphatic carboxylate counterions. The slopes $\Delta(\Delta G_{M,25})/\Delta m$ as summarized in Table 2 represent the variation of $\Delta G_{M,25}$ between two gemini n -alkyl-carboxylate with increasing chain length m .

Table 2. CMC, α_a , $\alpha_{b,25}$, $\Delta G_{M,25}$, and $\Delta G_t(\text{CH}_2)$ of Gemini 14-2-14 with Alkylcarboxylate Counterions

gemini	CMC (mM)	α_a	$\alpha_{b,25}$	$\Delta G_{M,25}$ (kJ·mol ⁻¹)	$\Delta(\Delta G_{M,25})/\Delta m$ (kJ·mol ⁻¹)
14C1	0.58	0.43	0.33	-20.88	
14C2	0.61	0.48	0.33	-20.65	0.23
14C3	0.42	0.54	0.36	-20.99	-0.34
14C4	0.35	0.52	0.38	-21.46	-0.47
14C6	0.23	0.37	0.29	-24.24	-1.39
14C8	0.12	0.10	0.11	-30.39	-3.08

low polarizability from what is expected from its hydrophobicity (between BR and I), whereas PH has very high polarizability and very low n_H . C₂ shows intermediate behavior with high pK_a and polarizability.

Anion Properties and CMC, Entropy Gain upon Micellization, The Role of Hydration, Polarizability, pK_a , and Ion Hydrophobicity. Figure 8 compares six different properties of small counterions X with the CMC of the corresponding gemini 14X. Again, it is observed that all the physical properties of the ions correlate to their CMCs as long as the ions preserve the same electronic configuration and same spherical morphology, such as halides counterions. The values that increase with CMC are the hydration energy (Figure 8C), hydration number n_H (Figure 8D), and the pK_a (Figure 8F). On the other hand, the partial molar volume v_s (Figure 8A), the polarizability

Table 3. CMC Measured at 30 °C unless Otherwise Noted, Ionization Degrees $\alpha_{b,25}$, and Free Energy of Micellization $\Delta G_{M,25}$ at 30 °C of 14-2-14 with Aromatic and Orphan Carboxylate Counterions

gemini	CMC (mM)	α_a	$\alpha_{b,25}$	$\Delta G_{M,25}$ (kJ·mol ⁻¹)
14SAL	0.09 (60 °C)	0.14		
14BENZ	0.14 (60 °C)	0.47		
14MHB	0.18 (60 °C)	0.45		
14PA	0.19 (60 °C)	0.43		
14MAND	0.23 (60 °C)	0.44		
14PHB	0.32 (60 °C)	0.41		
14DHB	0.37 (60 °C)	0.42		
14TART	0.06	0.42	0.33	-20.47
14PA	0.12	0.46	0.30	-26.07
14MAND	0.13	0.47	0.30	-25.95
14TFA	0.14	0.50	0.38	-23.95
14LACT	0.19	0.40	0.29	-24.96
14MeOAc	0.61	0.68	0.45	-18.70

(Figure 8B), and the lyotropic number N (Figure 8E) decrease with increasing CMC.^{15d,e,57,58}

Very interestingly, the loss of correlation between ion properties and their hydrophobicity as discussed in the previous section for polyatomic nonspherical anions appears related to the deviation from the linear correlation between the CMC and the physical properties. Let us consider gemini 14PH compared to gemini halides. PH is a highly hydrophilic anion with a largely negative free energy of hydration ΔG_{hyd} very similar to F (see Table 4). The values of ΔG_{HB} and relatively high pK_a are other properties which are common between PH and F. These hydrophilic properties are unfavorable for micellization, which explains in part the high CMC of 14PH. However, the CMC of 14PH (1.2×10^{-3} mol/L) is twice as high compared to 14F (6×10^{-4} mol/L), which indicates the presence of additional effects which further disfavor the micellization of 14PH. To understand this phenomenon, it is important to clarify the positive and negative contributions to driving forces of micellization.

Hydrophobic effect associated with the chain association¹⁶ is the primary driving force in micellization by promoting the release of water molecules which solvate the apolar chain. The spontaneous assembly of amphiphile monomers, classically called the hydrophobic effect, is driven by a net entropy increase of the whole solution. The antagonistic balancing force is the electrostatic force between the amphiphile headgroups with their counterions and water at the surface of the micelle. Hydrated and charged headgroups and counterions in solution can associate reversibly to form polar and neutral ion pairs that are less

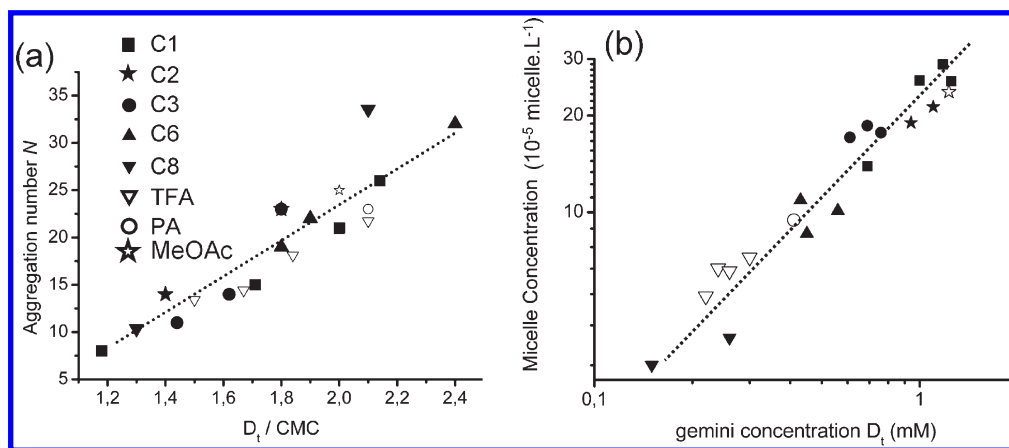


Figure 7. (a) Aggregation numbers and (b) Micelle concentration $[\text{Mic}]$ plotted as a function of D_t/CMC and total surfactant concentration D_t , respectively, for micelles of 14-2-14 with carboxylate counterions: (▼)C8, (▽) TFA, (○) PA, (▲) C6, (●) C3, (★) C2, (■) C1, (☆) MeOAc.

Table 4. Physical Properties for Small Anions: v_s , n_H , $-\Delta G_{\text{hyd}}$, α , ΔG_{HB} , N , and $\text{p}K_a$ at 25 °C^a

ion	v_s (cm ³ ·mol ⁻¹)	α (Å ³)	n_H	$-\Delta G_{\text{hyd}}$ (kJ·mol ⁻¹)	$\log P_{\text{calc}}$	ΔG_{HB} (kJ·mol ⁻¹)	N	$\text{p}K_a$
I	41.7	7.51	1.6	283	1.04	-1.09	12.5	-11
NO ₃	34.5	4.13	2.0	306	0.21	-0.68	11.6	-1.3
BR	30.2	4.85	1.8	321	0.63	-0.80	11.3	-9
CL	23.3	3.42	2.0	347	0.54	-0.61	10.0	-7
C ₂	46.2	5.50	2.2	373	0.09	0.12		4.8
PH	34.6	5.79	1.8	473	-0.77	-0.10	8.2	2.2
F	4.3	0.88	2.7	472	0.23	0.08	4.8	3.2

^a v_s , α , n_H , $-\Delta G_{\text{hyd}}$, and ΔG_{HB} values from ref 51 (values obtained using molar refractivity); N values from refs 52 and 53; $\text{p}K_a$ values from refs 54–56. To compare the different ions, only values from the same references are presented for each property.

hydrated than free ions. This leads to the release of water into the bulk with entropy increase. These interactions obviously depend on the hydrophobicity of the counterions. Hydrophobic counterions interact more strongly with an amphiphilic micellar interface, which results in stronger ion-pair formation, favors micelle formation, and decreases the CMC. However, if two ions with similar hydrophobicity are compared, other parameters which are directly linked to the entropy gain upon ion-pair formation must be considered. As we have pointed out previously, among the physical properties of F and PH (Table 4), their size ($V_{\text{PH}} = 34.6 \text{ cm}^3 \cdot \text{mol}^{-1} \gg V_{\text{F}} = 4.3 \text{ cm}^3 \cdot \text{mol}^{-1}$), the polarizability ($\alpha_{\text{PH}} = 5.79 \gg \alpha_{\text{F}} = 0.88$), and hydration number ($n_{\text{H,PH}} = 1.8 < n_{\text{H,F}} = 2.7$) are those which clearly differentiate PH from F; all are related to the large size of PH. Indeed, for these parameters, PH ions are more similar to ions such as BR or I. These differences in ion properties are likely the origin for the very high CMC value of 14PH.

Briefly, ions with high hydration numbers result in the high entropic gain for surfactant aggregation. Although the hydrophobicity of an ion does not alone favor micellization, the increased

hydration of the counterion does promote micellization (thus lowering the CMC) for entropic reasons.^{14d} PH ions which are large, hydrophilic but highly polarizable and weakly hydrated, are thus more unfavorable toward micellization and lead to higher CMC than highly hydrated F. Acetate ions, C2, which are relatively hydrophilic ($\Delta G_{\text{hyd}} \approx \Delta G_{\text{hyd}}$ of CL), but large ($V_s \approx V_s$ of I), have more modest, but similar properties; high polarizability ($\alpha \approx \alpha$ of BR) and intermediated hydration ($n_H \approx n_H$ of CL) with a high CMC ($\sim \text{CMC}$ of F). Conversely, the combination of relatively high hydration and strong hydrophobicity ($\Delta G_{\text{hyd}} = -306$, between those of BR and I) of NO₃ does not lower the CMC of 14NO₃ ($\sim \text{CMC}$ of 14BR). Here, it seems that other parameters such as its relatively low polarizability and high $\text{p}K_a$ disfavor ion-pair formation and decrease the entropy gain upon micellization, leading to higher than expected CMC values for 14NO₃.

Micellization of 14-2-14 with Aliphatic Carboxylate Counterions. The CMC, ionization degree, and free energy of micellization reported in Figure 5B and Figure 6 present a maximum for $m = 2$ –4. This behavior has been observed in other studies involving n -alkyl carboxylate or n -alkylsulfonate anions with cationic surfactants.^{26,27a,46,59,60} Anacker and Underwood¹³ have also observed the maximum of CMC for $m = 2$ in their study of the micellization of DTAB with sodium salts of n -alkylcarboxylates NaC_m. Moreover, Thalody and Warr^{59a} as well as Lissi et al.^{59b} reported that the selectivity coefficient of n -alkyl carboxylates for cationic surfactants is also minimal for $m = 2$ and that it increases for $m = 5$.

The effect of alkylcarboxylate alkyl chain length on their ion properties is shown in Table 5. Hydrophobicity of n -alkyl carboxylate anions is characterized by $\Delta G_{\text{transNB} \rightarrow \text{W}}$, the free energy of hydration ΔG_{hyd} .⁶¹ It is clear that not only the overall hydrophobicity but also its electronic nature is modified as it is reflected by their $\text{p}K_a$. The $\text{p}K_a$ of C1 is more than one unit lower than those of other n -alkyl carboxylates. The comparison between hydration numbers n_H , $\Delta G_{\text{transNB} \rightarrow \text{W}}$, ΔG_{HB} , and $-\Delta G_{\text{hyd}}$ of C1 and C2^{25,51,62} indicates that despite the presence of the methyl

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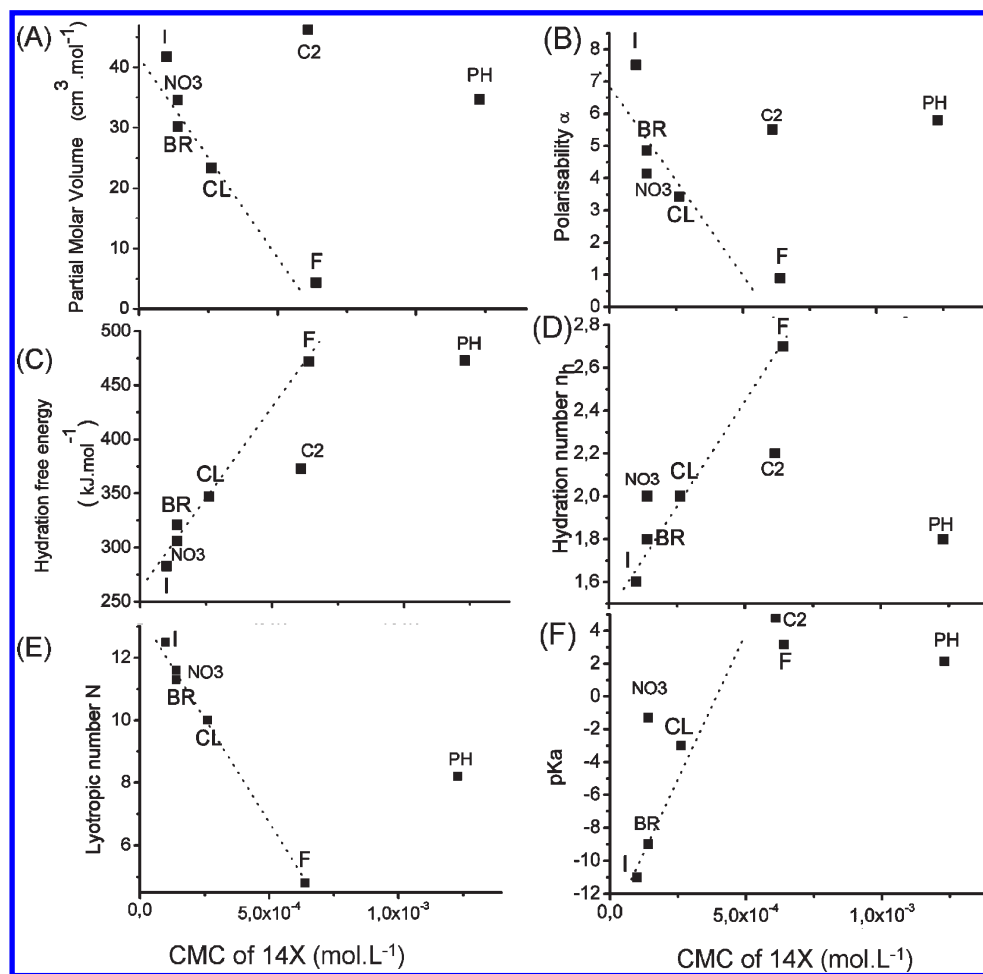


Figure 8. (A) Partial molar volume v_s ,⁵¹ (B) polarizability (α),⁵¹ (C) hydration free energy (ΔG_{hyd}),⁵¹ (D) hydration number (n_H),⁵¹ (E) lyotropic number (N),^{52,53} (F) pK_a ⁵⁴ as a function of the CMC of 14-2-14 with small counterions. The lines follow the evolution of physical properties of the gemini halides.

Table 5. pK_a , $-\Delta G_{\text{transNB} \rightarrow \text{W}}$ (the Free Energy of Transfer from Nitrobenzene to Water), and $-\Delta G_{\text{hyd}}$ of n -Alkyl Carboxylates $\text{C}_{m-1}\text{H}_{2m-1}\text{COO}^-$ (C_m)^a

ion	pK_a	α (\AA^3)	n_H	ΔG_{HB} ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta G_{\text{NB} \rightarrow \text{W}}^\theta$ ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔG_{hyd} ($\text{kJ}\cdot\text{mol}^{-1}$)	$\log P_{\text{calc}}$ (exp)
C1	3.75	3.7	2.1	−0.33	−30.6	−403	−0.46 (−0.54)
C2	4.76	5.5	2.2	0.12	−30.1	−373	0.09 (−0.17)
C3	4.86				−28.0	−376	0.58 (0.33)
C4	4.83				−26.3		1.07 (0.79)
C6	4.85				−18.1		2.05 (1.92)
C8	4.89				−12.6		3.03 (3.05)
C10	4.9				−13.6		4.02 (4.09)

^a Values for pK_a taken from ref 54; values for α and $\Delta G_{\text{NB} \rightarrow \text{W}}^\theta$ taken from ref 64; values for ΔG_{hyd} taken from ref 51.

group, C2 is slightly more hydrated and more kosmotropic than C1, while C1 is more hydrophilic. It was shown that the kosmotropicity continues to increase with alkyl chain length until $m = 4$ – 5 ,⁶³ after which water molecules are only used for the solvation of additional methylene units.

The free energy variation of micellization per methylene $\Delta(\Delta G_{\text{M},25})/\Delta m$ as shown in Figure 6 is positive between C1 and C2 before becoming negative at $m \geq 3$ reaching $−3.0 \text{ kJ}\cdot\text{mol}^{-1}$ between $m = 6$ and 8. This reflects that the addition of extra methylenes does not contribute equally for micelle formation; for

the short chains ($m < 4$), the chain elongation has very little effect on the $\Delta G_{\text{M},25}$. The micellization of 14-2-14 C2 is less advantageous than that of 14-2-14 C1. Only for the chains longer than C4 does the free energy of micellization clearly decrease with increase in chain length (Figure 6). The free energy for the transfer of a methylene unit from water to an organic phase $\Delta(\Delta G_{\text{M},25})/\Delta m$ is $−3.7 \text{ kJ}\cdot\text{mol}^{-1}$, a value close to $\Delta(\Delta G_{\text{M},25})/\Delta m$ for $m = 6 \sim 8$. This indicates that almost all the methylenes added after $m = 6$ are embedded in the apolar domain of the micelle.⁴⁶ A similar observation has been reported with decylammonium micelles with organic counterion C_m by ^1H NMR.⁶⁵

Altogether, two opposing effects seem to play antagonistic roles when the alkyl chain length of the counterion is increased,

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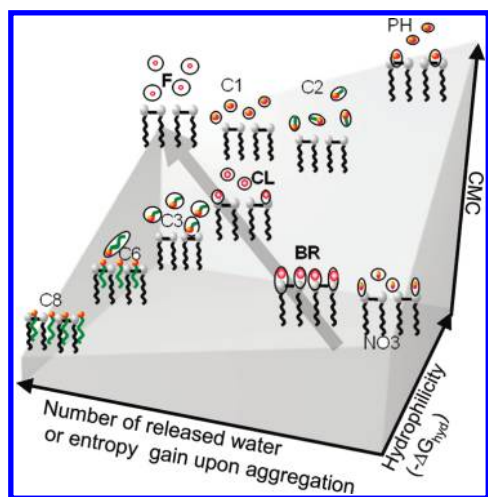


Figure 9. Schematic representation of CMC evolution (vertical axis) which depends both on hydrophilicity of anions and entropy gain upon aggregation. CMC increases with hydrophilicity of the counterions, meanwhile it decreases with the entropy gain upon aggregation. For the halide ions, the more hydrophilic the ions are, the higher is the entropy gain, whereas for alkylcarboxylate anions, the tendency is the opposite. Phosphate anion is an interesting example as it is very hydrophilic but poorly hydrated. Filled cycles are the ions with various sizes. Open black cycles represent the hydration sphere around anions.

both of which are entropy driven processes. First, adding a methylene unit to the C1 counterion increases its size and its kosmotropic character. These effects tend to separate the counterion from the micellar surface which is altogether unfavorable to ion-pair formation and to micelle formation (increase of CMC, ionization degrees α , and free energy of micellization $\Delta G_{M,25}$). Meanwhile, the hydrophobicity of the counterion also increases with the chain length, and, at $m \geq 3$, this effect dominates the increase in kosmotropy. The counterion becomes more embedded in the apolar micellar core, and more water molecules are released when the micelle is formed. These effects promote micellization and are responsible for the decrease of the CMC, α , and $\Delta G_{M,25}$ as observed for longer-chain counterions. This balance leads to the presence of a maximum or minimum of the CMC, ionization degrees, and free energy of micellization at a given chain length m of n -alkyl carboxylate counterions.

Counterion Hydrophilicity and Hydration Effects on CMC. Figure 9 presents a schematic view of the CMC of the 14-2-14 X as a function of the energy of hydration ΔG_{hyd} and the entropy gain upon aggregation of the counterion. The figure illustrates that the micellization does not depend on one single parameter that describes ion properties but on the combined effect of multiple ionic properties. The entropy gain is controlled by the propensity of the counterions to form ion pairs with surfactant headgroups as well as by the number of the released water molecules upon aggregation.

Therefore, the hydrophilicity of ions (as described by free energy of hydration ΔG_{hyd}) cannot alone explain the CMC values, but the combined effect with ion size and kosmotropy, pK_a , and the hydration of the counterion need to be considered. For halide anions, the smaller the ionic radius R of an ion is, the higher is the hydrophilicity, the hydration number n_H , and the CMC. On the other hand, for the polyatomic anions such as PH, C2, and NO_3 , their n_H , ionization degree, pK_a , and ion size have effects on the entropy of micellization and cause the CMC values to deviate. The CMCs of 14-2-14 X gemini with aliphatic carboxylate counterions are also represented in the same figure. For this family, the

Table 6. Physical Properties of Aromatic Carboxylate Ions: pK_a , Experimental and Calculated $\log P$, and $-\Delta G_{hyd}$ at 25 °C^a

anion	pK_a	$-\Delta G_{hyd}$ (kJ·mol ⁻¹)	$-\Delta G_{hyd}$ (kJ·mol ⁻¹)	$\log P_{exp}$ ($\log P_{calc}$)
MAND	3.85			0.62 (0.57)
DHB	4.04			0.86 (0.91)
PA	4.28		314.6	1.41 (1.43)
MHB	4.06	245.3		1.5 (1.39)
PHB	4.48	254.1		1.58 (1.39)
BENZ	4.19	242.4	297.1	1.87 (1.87)
SAL	2.98	213.5		2.26 (2.24)

^a Values for pK_a taken from ref 54; values for ΔG_{hyd} (MAND, DHB, MHB, PHB, SAL) taken from ref 66; values for ΔG_{hyd} (PA and BENZ) taken from ref 62; values for $\log P_{exp}$ and $\log P_{calc}$ taken from ref 68.

increasing alkyl chain length is accompanied on one hand by increased hydrophobicity, but on the other hand with increasing kosmotropic effect⁶³ due to the structuring of water around the apolar chains. Although C2 ions are highly hydrated and have high polarizability, they do not tend to form ion pairs with surfactant headgroups due to their kosmotropicity. Therefore, the entropy gain upon micellization is small, which leads to a similar effect as poorly hydrated and highly polarizable PH ions, that is, particularly high CMC.

Aromatic Carboxylate Counterions: Effect of Counterion Morphology on Micellization.

All the anions of this family are carboxylate anions with an aromatic cycle in their structure. However, their physical properties show important variations. Table 6 presents selected physical properties of the aromatic carboxylate anions chosen for this study.⁶⁶ Phenylacetate (PA) and mandelate (MAND) are distinct from the benzoate-derived counterions because the latter present mesomeric structures with delocalized negative charge which make the anions more hydrophobic, whereas for PA and MAND the negative charge remains localized on the carboxylate moiety. Among the benzoate-derived anions, the hydrophobicity reflects the number and the position of the hydroxyl groups. Hydrophobicity derived both from $\log P_{exp}$, $-\Delta G_{hyd}$, or $-\Delta G_{NB-W}^0$ increases in the order MAND < DHB < PHB \approx MHB < PA < BENZ < SAL. It is important to note that the hydrophobicity does not relate directly to pK_a : salicylic and mandelic acids both have much lower pK_a values than other anions (2.98 and 3.85) due to the intramolecular hydrogen bond which stabilizes the anionic form.⁶⁷ This effect is stronger for salicylate due to its planar geometry preventing the rotation of the carboxylate and further stabilizes the hydrogen bond. Another consequence of the intramolecular hydrogen bond in salicylate is its strong hydrophobicity in spite of the presence of the hydrophilic hydroxyl group. On the other hand, mandelate is very hydrophilic despite its low pK_a , which reflects the fact that in this case the intramolecular hydrogen bond cannot isolate the anion from the contact of water.⁶⁶

The analysis of the CMC of gemini 14-2-14 with benzoate counterions shows that it tracks mainly with the hydrophilicity of the counterions (see Results section and Table 3). However, the correlation between the hydrophilicity of the counterions and the value of CMC is not as good if we include the PA and MAND anions. Indeed, while MAND is the most hydrophilic anion, the CMC of 14MAND is lower than those of 14PHB and 14DHB. This is likely explained by interfacial packing of counterions.

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(67) This effect is stronger for salicylate due to its planar geometry preventing the rotation of the carboxylate and further stabilizes the hydrogen bond.

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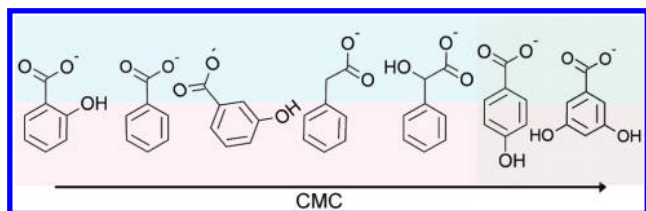


Figure 10. Aromatic counterions at cationic micellar interface. Illustration inspired from ref 26.

As shown by Bijma and Engberts²⁶ for SAL, MHB, and PHB, the position of the hydroxyl group with respect to the carboxylate is very important for the micellar stability: if the OH group is located inside the apolar core of the micelle, then micelle formation is less favorable.

While MHB can tilt to lower repulsion between the hydroxy group and the apolar micellar domain, this is more difficult to achieve with PHB and DHB, which disfavor ion-pair formation with cationic headgroups, and micelle formation. This explains why 14PHB and 14DHB have much higher CMC values than what would be expected from their hydrophobicity (Figure 10).

Effect of Substituents on the Counterion. Other comparisons between the counterions in Chart 1 allow insight onto the impact of selected chemical structure modifications of the counterion on the micellization of 14-2-14: (1) Replacement of the terminal methyl group of an alkyl carboxylate by an aromatic group generally results in a decrease of the CMC due to the increased hydrophobicity (e.g., 14C3 vs 14PA, or 14C2 vs 14BENZ). (2) Comparing trifluoroacetate (TFA) to acetate (C2) underscores the higher hydrophobicity of the trifluoro substituent effect (Table 7). (3) The CMC of MeOAc with respect to C4 demonstrates the effect of replacing a methylene by an oxygen, leading to a largely higher CMC of 14MeOAc compared to 14C4 (Table 7). Interestingly, the CMC of 14LACT is significantly lower than that of 14C3, although lactate is much more hydrophilic than C3. The formation of intramolecular hydrogen bonding decreases the CMC value as was also observed with BENZ versus SAL. (4) The CMC of 14TART is one-third that of 14LACT despite the higher hydrophilicity of the tartrate ion, indicating that the doubled charge of the counterion reduces the CMC due to the stronger electrostatic interaction with cationic surfaces.

Aggregation Number of Micelles and the Molecular Structure of Gemini Surfactants. In terms of morphology, our data demonstrated that micelles formed with a variety of counterions share similar properties when normalized concentrations (D_i/CMC) are used. The data, obtained for gemini surfactants with same chain length, is valid for micelles that remain spherical ($< 2CMC$). The aggregation numbers of these micelles fall within a very narrow range, systematically increasing with concentration regardless of their apparent charges and ionization degrees. This is very interesting, especially when we consider that both the ionization degree $\alpha_{b,25}$ and the CMC show more than 4-fold variation, from 0.1 to 0.45 for $\alpha_{b,25}$ and from 0.14 to 0.68 mM for the CMC. Thus, the level of ionization of the micelles has little, if any, effect on the aggregation numbers of micelles as a function of normalized concentration.⁶⁹ Consequently, at the same surfactant concentration D_i , the size of a micelle depends strongly on the properties of the counterions. The hydrophobic counterions lower the CMCs and favor bigger micelles with

(69) It is worth noting that even for micelles having long hydrocarbon counterions (C8) we observed the same tendencies, although we have independently shown that these counterions are fully embedded in the micellar cores. This means that hydrophobic core volume of 14-2-14 C8 micelles should be larger than other 14-2-14 micelles by approximately 50%.

Table 7. Physical Properties of Orphan Anions and Some Carboxylates: pK_a and Calculated $\log P_{calc}$ of Corresponding Carboxylic Acids and $-\Delta G_{hyd}$ at 25 °C^a

anion X	pK_{a1} (pK_{a2})	CMC of 14X (mM)	$-\Delta G_{hyd}^1$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\log P_{calc}$ ($\log P_{exp}$)
C1	3.75	0.58	403	-0.46 (-0.54)
TFA	0.23	0.14	251	0.50
C2	4.76	0.61	373	0.09 (-0.17)
LACT	3.87	0.19	288	-0.65 (-0.72)
TART	2.98 (4.34)	0.06		-1.00
C3	4.86	0.42	376	0.58 (0.33)
MeOAc	3.54	0.61	325	-0.68
C4	4.83	0.35		1.07 (0.79)

^a Values for pK_a taken from ref 54; values for ΔG_{hyd} taken from ref 51; values for $\log P_{calc}$ taken from ref 68.

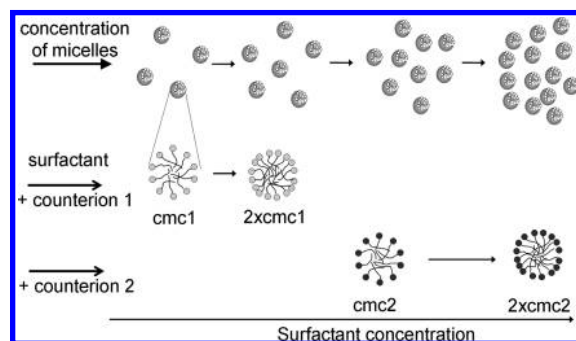


Figure 11. Schematic representation of how the aggregation numbers and the concentration of micelles vary for two gemini surfactants (dark and light gray) with different counterions with high and low CMC (cmc2 and cmc1, respectively). Aggregation numbers of micelles depend on the surfactant concentration with respect to their cmc, whereas the concentration of micelles depends on the absolute surfactant concentration.

higher aggregation numbers compared to hydrophilic counterions at a given concentration. On the other hand, the number of micelles depends very little on the nature of the counterion. Whatever the counterion type, its ionization degree, or the CMC, the concentration of the micelles seems to depend linearly only on the total surfactant concentration.

To sum up, the gemini surfactants with hydrophobic counterions in general form micelles at low surfactant concentration (low CMCs) with low aggregation numbers (~ 20) and with low micellar concentration, whereas counterions which have high CMCs also start to form micelles with identical aggregation numbers, but at high surfactant concentrations (high CMC) and already at high micellar concentrations as shown with a schematic representation in Figure 11. In conclusion, it would seem that the concentration of micelles is solely determined by entropy.

Conclusion

We have performed a comprehensive study of the ion specific effect of counterions on the micellization of cationic gemini surfactant 14-2-14. Counterions were classified into four different families, and within each family several effects were distinguished according to the counterion's chemical structure. As expected, the hydrophilicity of the ions is the primary effect determining micellization: The higher the hydrophilicity of a counterion, the more unfavorable micellization becomes, leading to high CMCs. The family of aliphatic carboxylates offers a particularly remarkable

correlation between the hydrophilicity of the counterion and the CMC of the gemini surfactant.

Meanwhile, this broad study clearly demonstrates the importance of other parameters which influence micellization, particularly the hydration of the counterion and the resulting entropy variation during aggregation due to the release of water molecules. For monatomic anions such as halide anions, the hydration number is directly related to the hydrophilicity: The more hydrophilic the anions are, the smaller the polarizability is, and the higher the hydration number is. However, for the polyatomic anions, this is no longer the case. For example, a large but very hydrophilic anion such as PH has a relatively high polarizability and a small hydration number. When compared to ions with similar hydrophilicity but with a higher number of hydration (such as F), the micellization of 14PH is further disfavored, most likely due to entropic reasons. This is a typical example that the polarizability of the anions alone cannot be correlated to their hydrophilicities and the CMC values. This additional entropic effect is also clearly observable for the variation of the CMCs of 14-2-14 with *n*-alkyl carboxylate counterions when the chain length is increased. While the hydrophobicities of the anions show a monotonous increase with increasing chain length, the opposing kosmotropic effect initially overcomes the entropic gain, leading to a maximum of the CMC values vs chain length at short chain lengths.

The investigation of aromatic carboxylate anions and orphan anions has provided some additional insights. First, the presence of an aromatic cycle or replacement of hydrocarbon by fluorocarbon results systematically in a decrease of the CMC primarily due to the higher hydrophobicity, but also in certain cases to the resonance stabilization of the negative charge (as in the case of benzoates). While the addition of oxygen increases the hydrophilicity of the anions, any resulting intramolecular hydrogen bonds have important effects in decreasing the hydration of the anions and stabilize the micelles (therefore lowering the CMC, as was observed with salicylate, mandelate, or lactate). The position and the number of hydroxyl substituents of the aromatic counterions also influence the micellization for steric reasons: When the hydroxyl group is *ortho* to the carboxylate of the aromatic anion, micellization is stabilized, whereas it can be destabilized if it is placed *para* to the carboxylate.

The ensemble of our observations clearly demonstrates that these opposing effects (e.g., ion hydration, ion polarizability,

intra-intermolecular hydrogen bonds, and steric hindrance) all affect the entropy gain upon micellization and the propensity of the counterions to form ion pairs with the amphiphiles head-groups. In other words, ion pairing cannot be accurately described using one single parameter, but requires an ensemble of several parameters. This is why, for example, two ions with similar hydrophilicity but with different hydration and/or with different steric effect may lead to very different CMCs. Indeed, by using different families of anions and varying independently the effect of various ion properties (ion type (Hofmeister), hydrophobicity, hydrogen bonding, and substitution) we could unambiguously demonstrate how such effects can cooperatively affect the propensity of counterions to form ion pairs with surfactant head-groups and alter the entropic energy gain upon micellization. These results provide new insight into understanding the effect of ions on the delicate balance of forces controlling aggregate morphology and solution properties of charged amphiphilic molecules.

The investigation of the aggregation number and the concentration of micelles revealed intriguing micellar properties. Regardless of the absolute CMC values and the ionic properties which show an important variation with the counterions, the aggregation number of micelles just above the CMC depends only on the normalized concentration D_t/CMC as long as the molecular structure of the cationic moieties of gemini surfactant is fixed and spherical micelles are considered. On the other hand, the concentration of the micelles depends on the absolute concentration of the surfactant, that is, at a given concentration above the CMC, all the gemini 14-2-14 studied have the same number of micelles per volume which increases with the surfactant concentration indicating that this process is primarily controlled by entropy.

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Supporting Information Available: Ion exchange methods; typical fluorescence spectra and dependence $\ln(I/I_0)$ versus quencher concentration for different D_t ; details of stability problems for 14F. This material is available free of charge via the Internet at <http://pubs.acs.org>.