J Surfact Deterg (2018)
DOI 10.1002/jsde.12241

ORIGINAL ARTICLE

The Effect of Polar Head and Chain Length on the Physicochemical Properties of Micellization and Adsorption of Amino Alcohol-Based Surfactants

Zakaria Hafidi[1] · **Mohammed El Achouri**[1]

Received: 30 April 2018 / Revised: 10 October 2018 / Accepted: 19 November 2018
© 2018 AOCS

In this work, we have synthesized a series of quaternary ammonium from amino alcohols and n-bromoalkanes. The compounds are referred to as C_nEtOH, C_nPrOH, and C_niPrOH (where n = 12 and 14 carbons, EtOH = ethanol, PrOH = propanol, iPrOH = iso-propanol). Their structures were checked using the usual spectroscopic methods [^{1}H, ^{13}C nuclear magnetic resonance (NMR) and infrared (IR)]. Their physicochemical properties in aqueous solution were studied using conductivity, surface tension, and ultra violet (UV)–visible absorption spectroscopy measurements. This study was conducted to show the effect of the linear hydrophobic chain and the location of the OH polar group with respect to the N^+ quaternary ammonium on the physicochemical properties of the surfactants. The comparison between the physicochemical properties of the surfactants studied shows a distinct effect of the position of the OH group on the critical micelle concentration (CMC), the ionization degree (α), the area occupied at the interface ($A_{\min}$), the free energy of adsorption (ΔG^0_{ad}), and the free energy of micellization (ΔG^0_M). The intermolecular interaction between the synthetic surfactants and the methyl orange (OM) dye is related to the degree of hydration of the micelle, proven by the hypsochromic displacement of OM wavelength ($\lambda_{\max}$) and ionization (α) of the micelles. The CMC, the degree of ionization, and the degree of hydration of the micelle follow the same trend.

Keywords Surfactants · Quaternary ammonium · Polar head group · Critical micelle concentration · Degree of ionization · Surface excess concentration · Amino alcohol

J Surfact Deterg (2018).

Introduction

Cationic surfactants have attracted the attention of many researchers for a long time because of their wide applications, they are used as softeners, cosmetic or coating ingredients (Akram et al., 2015), antimicrobial agents (Gotmukle and Bhagwat, 2013; Migahed et al., 2016), and also in the mining and papermaking industries (Nilsson et al., 2008).

The aggregation of surfactants in micellar structures is a phenomenon that depends on the molecular structure of the surfactant and the conditions of the surfactant solution (Akram et al., 2015; Grillo et al., 2009; Lv et al., 2014; Pan et al., 2012; Phani Kumar et al., 2011, 2018; Prameela et al., 2013, 2015, 2017; Wattebled and Laschewsky, 2007). The formation of micelles for ionic surfactants in solution is mainly controlled by the equilibrium between two opposing forces such as the attractive interaction between the linear hydrophobic chains and the electrostatic repulsion between the ionic groups (Akram et al., 2014; Maiti et al., 2009).

The modification of the molecular structures of the surfactants and the modification of the conditions of the surfactant solution affect the two antagonistic forces, thus influencing the micellization and also the adsorption of the ionic surfactants (Kabir-ud-Din et al., 2008; Moreira and Firoozabadi, 2009; Shah et al., 2016).

In the literature, there are numerous reports on the effects of the alkyl chain length on the micellization of surfactants

---

✉ Mohammed El Achouri
achmedens@yahoo.fr

[1] Mohammed V University in Rabat, Laboratoire de physico-chimie des matériaux inorganiques et organiques, Centre des Sciences des Matériaux, Ecole Normale supérieure-Rabat, Morocco

containing a single hydrophilic group. On the other hand, only a limited number of publications have been devoted to bifunctional species and the effect of the polar head on micellization. The influence of the size of the hydrophilic part of a quaternary ammonium surfactant on its ability to adsorb at the air/water interface and to form micelles in aqueous media has been reported by many researchers (Dahanayake and Rosen, 1984; Kabir-ud-Din et al., 2008; Moreira and Firoozabadi, 2009; Omar and Abdel-Khalek, 1998; Shah et al., 2016; Venable and Nauman, 1964), but the study of the effect of the localization of a polar group with respect to quaternary nitrogen, N^+, has not been widely reported. Let us cite, for example, the work of Chevalier et al. (1991), who studied the effect of the distance between the positive group N^+ and the carboxylate group on the physicochemical parameters, such as the maximum surface excess Γ_m and critical micelle concentration (CMC) of zwitterionic surfactants and also the work in which Hajji et al. (1990) showed the effect of the polar head of 2-(decyldimethylammonio) alkanol bromide surfactants on physiochemical parameters such as the degree of ionization, α, and CMC.

The present article deals with surfactants prepared from amino alcohols, whose polar heads contain two incorporated functional groups: ammonium, N^+, and alcohol, OH. The aim of this work is to detect micelle formation and investigate the effect of the polar head on the properties accompanying the micellization using different techniques, such as conductivity and surface tension measurements. The interactions of those cationic surfactants with an anionic dye, methyl orange (OM), will also be used to understand the behavior of surfactants studied in aqueous solution better.

Experimental

Reagents

All solvents were of reagent grade and used without further purification, 3-(dimethyl amino) propan-1-ol (>99%), 1-(dimethyl amino) propan-2-ol (>99%), and 2-(dimethyl amino) ethan-1-ol (>99%) were purchased from Fluka, Swiss, 1-Bromododecane (>97%), 1-Bromotetradecane (>97%), methyl orange (Helianthin), Acetonitrile, Dichloromethane, Methanol, and Sodium bromide were from Sigma-Aldrich, Germany.

Synthesis

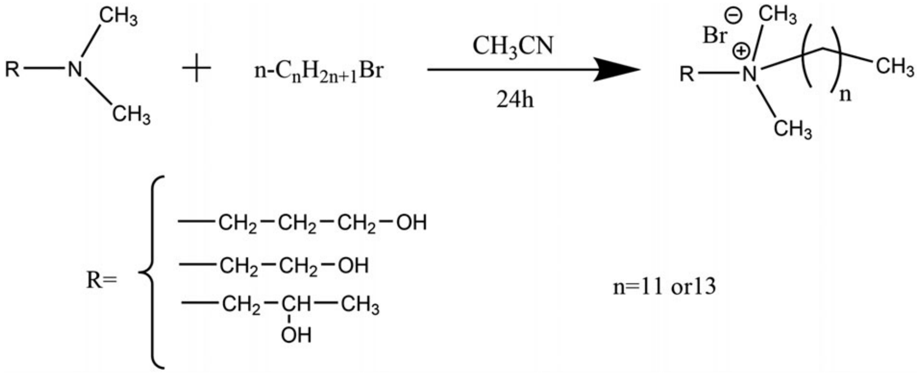
N-(hydroxyalkyl)-N,N- dimethyl n-alkyl ammonium bromides (Scheme 1), referred to as C_nEtOH, C_nPrOH, and C_niPrOH (n = 12 and 14, EtOH = ethanol, PrOH = propanol, and iPrOH = iso-propanol) were synthesized using a simple alkylation of the amino alcohol (3-(dimethyl amino) propan-1-ol, 1-(dimethyl amino) propan-2-ol, or 2-(dimethyl amino) ethan-1-ol)) with alkyl bromide (1-Bromododecane or 1-Bromotetradecane) in acetonitrile: a mixture of bromoalkane (25 mmol) and amino alcohol (20 mmol) in acetonitrile (20 mL) was heated for 24 h. The excess of amine was eliminated by vacuum evaporation. The products obtained were washed three times with a mixture of ether and hexane for purification. The yield of the reaction was about 70%.

The purity of the compounds was determined by chromatography, using a thin layer chromatography (TLC) plate on silica gel immersed in a solution of 8% of NaBr prepared in methanol. The eluent used was methanol/dichloromethane (1:9, by vol); the examination of the spots on the plate was done by the ultra violet (UV) light (245 nm) using bismuth nitrate as a revelator.

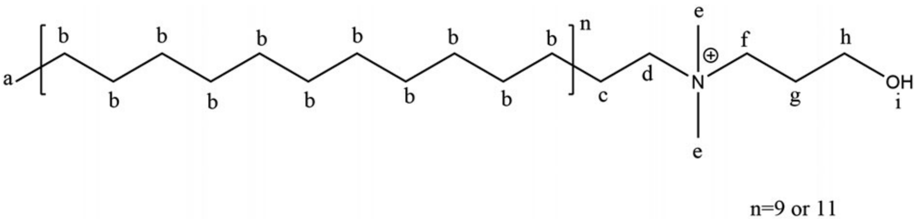
Structural Characterization

The structure of the pure component was verified by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), using a Varian spectrometer at 499.8 MHz (^{1}H) and 125.23 MHz (^{13}C), using the signal of deuterium of the solvent as the lock. Infrared spectra were recorded on a Spectrophotometer ALPHA II FTIR.

C_nPrOH (Scheme 2).



Scheme 1 Synthesis of N-(n-hydroxyalkyl)-N,N-dimethyl n-alkyl ammonium bromides



Scheme 2 The spectral characteristics—^{1}H and ^{13}C NMR spectra of *N-(3-hydroxypropyl)-N,N-dimethyl n-alkyl ammonium bromide*(C_nPrOH)

^{1}H NMR: (a) 0.89 ppm(t;3H); (b) 1.24–1.28 ppm (m;22H or 18H); (c) 1.59 ppm (p;2H); (d) 3.55 ppm (m;2H); (e) 3.34 ppm (s;6H); (f) 3.64 ppm (t;2H); (g) 1.88 ppm (p;2H); (h) 3.76 ppm (td;2H); and (i) 5.51 ppm (t;1H).

^{13}C NMR: (a) 14.09 ppm, (b; c; d) 22.71–65.04 ppm, (e) 51.62 ppm, (f) 62.04 ppm, (g) 27.95 ppm, and (h) 58.28 ppm.

IR: $\upsilon_{(O–H)}$ = 3746.4–3746.6 cm^{-1}; $\upsilon_{(C–H)}$ = 3000-3210 cm^{-1}; and $\upsilon_{(C–C)}$ = 740.8–1560.71 cm^{-1}.

C_nEtOH (Scheme 3).

^{1}H NMR: (a) 0.89 ppm (t;3H); (b) 1.24–1.28 ppm (m;22H or 18H); (c) 1.59 ppm (p;2H); ; (d;f) 3.58-3.60ppm (dt;4H); (e) 3.34 ppm (s;6H); (g) 3.89 ppm (q;2H); and (i’) 4.93 ppm (t;1H).

^{13}C NMR: (a) 14.09 ppm, (b; c; d) 22.71–65,56 ppm, (e) 51.81 ppm, (f) 66.58 ppm, and (g) 55.67 ppm.

IR: $\upsilon_{(O–H)}$ = 3734.2–3752.24 cm^{-1}; $\upsilon_{(C–H)}$ = 3009.2–3205.4 cm^{-1}; and $\upsilon_{(C–C)}$ = 739.4–1561.2 cm^{-1}.

C_niPrOH (Scheme 4).

^{1}H NMR: (a) 0.89 ppm (t;3H); (b) 1.24–1.28 ppm (m;22H or 18H); (c) 1.52–1.53 ppm (m;2H); (d) 3.45–-3.49 ppm (hept;2H); (e) 3.43 ppm (s;6H); (f) 3,15–3.65 ppm (dd;2H); (g) 4.29 ppm (m;1H); (h) 1.42 ppm (d;3H); and (i”) 5.23 ppm (d;1H).

^{13}C NMR: (a) 14.09 ppm, (b; c; d) 22.71–66.05 ppm, (e) 53.11 ppm, (f) 68.1 ppm, (g) 61.75 ppm, and (h) 20.81 ppm.

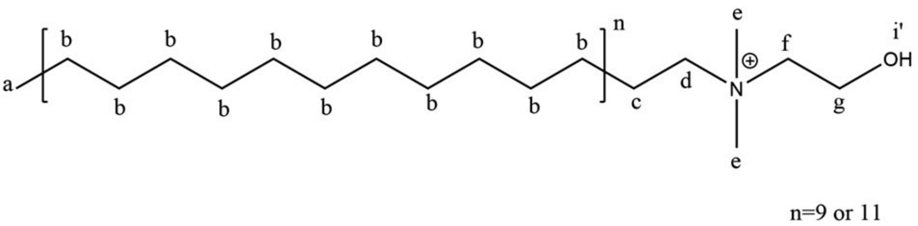
IR: $\upsilon_{(O–H)}$ = 3741.26–3877.08 cm^{-1}; $\upsilon_{(C–H)}$ = 3009.2–3387 cm^{-1}; and $\upsilon_{(C–C)}$ = 685.6–1591.2 cm^{-1}.

Conductivity Measurements

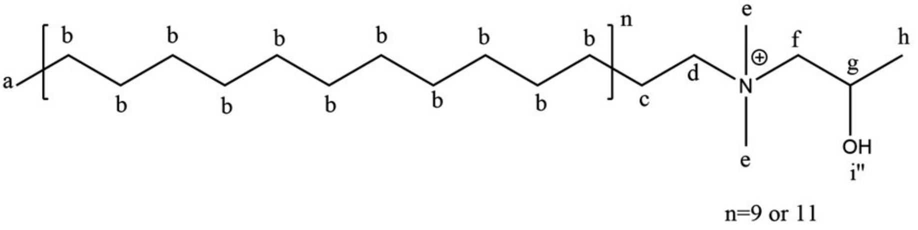
Conductivity measurements for the different concentrations of prepared surfactants are taken using Thermo Scientific Orion Star A212 Benchtop Conductivity Meter of a cell constant K equal to 0.4750 cm^{-1}. The aqueous solutions of surfactants were prepared with ultrapure water having a conductivity value of about 2 μS cm^{-1} at 298.15 K.

Surface Tension Measurements

The measurement of the surface tension (γ) for the solutions of different surfactant concentration was made by the plate method using a Lauda TD1 tensiometer with an accuracy of ±0.2 mN m^{-1}. The surface tension of the ultrapure



Scheme 3 The spectral characteristics—^{1}H and ^{13}C NMR spectra of *N-(2-hydroxyethyl)-N,N-dimethyl n-alkyl ammonium bromide*(C_nEtOH)



Scheme 4 The spectral characteristics—^{1}H and ^{13}C NMR spectra of *N-(2-hydroxyisopropyl)-N,N-dimethyl n-alkyl ammonium bromide* (CniPrOH)

water γ_W was 73.1 ± 0.2 mN m^{-1} at 298.15 K. Before each measurement, the aqueous solutions of surfactants in a concentration range from 1×10^{-6} to 1×10^{-1} mol L^{-1} were filtered on filter paper having a porosity of 0.45 μm.

Absorbance Measurements

The absorbance spectra of OM solutions at different concentrations were made using a Jasco V-630 UV–VIS Spectrophotometer with quartz cups. The change of the absorbance value in the range 300–600 nm in the presence of a surfactant was determined using water as a reference. All tests were conducted at ambient temperature and neutral pH.

Results

Conductivity Measurements

The plots obtained from the conductivity as a function of surfactant concentrations are presented in Fig. 1 for the C_{14} series. The same trend was observed for the C_{12} series. These conductometry diagrams allow calculation of the physicochemical parameters, such as CMC, degree of ionization, α, and free energy of micellization, ΔG_M^0.

The hypothesis of an aggregation of molecules in clusters beyond a threshold concentration was first suggested by McBain in 1913 (Holmberg, 2002). In water, the cationic surfactant molecules form micelles in which the hydrophobic parts assemble and are protected from contact with water by an envelope of polar heads. The CMC is frequently determined to be the concentration at the intersection of the two straight lines extrapolated from the experimental values of the conductivity before and after the CMC (κ_C< CMC, κ_C > CMC).

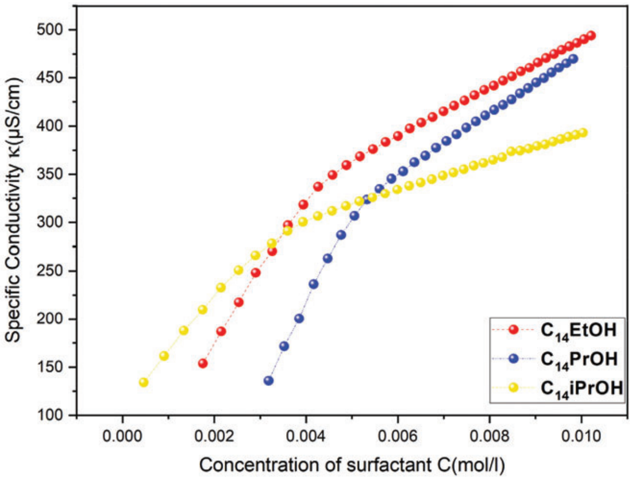


Fig. 1 Specific conductivity (κ) as a function of concentration of C_{14}EtOH, C_{14}PrOH, and C_{14}iPrOH at 298.15 K

The degree of ionization of a micelle (α) is defined as the fraction of counterion not associated with the micelle; in others terms, α quantifies the proportion of counterions that are completely hydrated away from the micelles compared to the counterion set. α can then be obtained by making the ratio of the slopes of the conductivity curve as a function of the concentration of surfactant before and after the CMC according to the following relation:

$$\alpha = \frac{S_2}{S_1} \tag{1}$$

where S_1 is the post-CMC slope and S_2 is the pre-CMC slope. The value of α also reflects a partial binding between the amphiphile molecules and the Br^- counterion and provides the net charge of the micelles. α can also be used to predict the degree of hydration of micelles (Soldi et al., 2000).

The free energy of micellization of a monovalent ionic amphiphile can be obtained from the CMC and the degree of ionization α (Nakagaki and Handa, 1984; Zana, 1996):

$$\Delta G_M^0 = (2+\alpha)\mathrm{R}Tln\left(\frac{\mathrm{CMC}}{\omega}\right) \tag{2}$$

where ω is the number of moles of water per liter (ω = 55.5 mol L^{-1} at 298.15). The results obtained from conductivity measurements are summarized in Table 1.

Surface Tension Measurements

Figure 2 shows the variation of the surface tension as a function of the concentration of surfactants. To determine the number of molecules adsorbed at the interface, we have used the method based on the measurement of the surface tension, γ, as a function of the concentration of surfactant according to the Gibbs adsorption equation (Rosen and Kunjappu, 2012):

$$d\gamma = \sum_i \Gamma_i d\mu_i \tag{3}$$

where Γ_i can be assimilated to the number of moles of each species, i per unit area at the interface (Holmberg, 2002), and μ_i is the chemical potential for each species, i.

$$d\gamma = -\mathrm{R}T\sum_i \Gamma_i dlnC_i \tag{4}$$

where R is the gas constant in J mol^{-1} L^{-1}, T the temperature in K, and C_i the concentration in mol L^{-1}. For ionic surfactants of the $AB_{\frac{|Z_A|}{|Z_B|}}$ type such that A is the surfactants of the charge Z_A and B the counterion of opposite charge Z_B, the equation is written in the following way:

Table 1 Conductivity parameters of surfactants at 298.15 K: Critical micelle concentration (CMC), ionization degree α, and free energy of micellization ΔG_M^0

	C_{12}PrOH	C_{12}EtOH	C_{12}iPrOH	C_{14}PrOH	C_{14}EtOH	C_{14}iPrOH
CMC (mmol L^{-1})	15.2	14.6	13.7	5.1	4.2	3.5
α	0.51	0.47	0.45	0.33	0.32	0.29
ΔG_M^0(kJ mol^{-1})	−30.28	−31.25	−31.89	−38.43	−39.54	−40.95

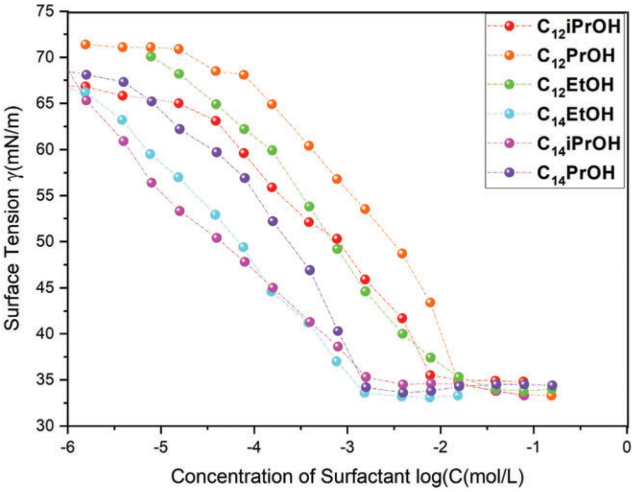


Fig. 2 Variation of the surface tension γ with surfactant concentration log(C) for C_nPrOH, C_nEtOH, and C_niPrOH (n = 12 and14) at 298.15 K

$$d\gamma = -\mathrm{R}T[\Gamma_A dlnC_A + \Gamma_B dlnC_B] \tag{5}$$

suppose that at the interface, the condition of the electroneutrality $\Gamma_B = \phi\Gamma_A$ is satisfied. Where ϕ is the charge ratio $\left|\frac{Z_A}{Z_B}\right|$

$$d\gamma = -(1+\phi)\mathrm{R}T\Gamma_A dlnC_A \tag{6}$$

the factor (1 + ϕ) is generally noted in the literature by n, thus the surface excess concentration at the air/water interface Γ_m can be written:

$$\Gamma_m = \frac{-\left(\frac{d\gamma}{d\log C_A}\right)}{2{,}303n\mathrm{R}T} \tag{7}$$

where $\left(\frac{d\gamma}{d\log C_A}\right)$ is the slope of the surface-tension plots just below the CMC.

The curve of the surface tension (γ) as a function of the concentration of surfactants is also used to determine the other physicochemical parameters such as minimum area per molecule, $A_{\min}$, surface pressure, Π_{CMC}, free energy of adsorption, ΔG_{ad}^0, and efficiency, pC_{20}.

The area occupied by molecules at the interface provides information on the degree of stacking and the orientation of the adsorbed surfactant molecule. This parameter, $A_{\min}$, is calculated by the following relation:

$$A_{min} = \frac{10^{16}}{N.\Gamma_m} \tag{8}$$

where N = Avogadro's number and Γ_m (mol cm^{-2}) is the maximum surface excess concentration at the CMC.

The efficiency pC_{20} is the negative logarithm ($pC_{20} = -\log(C_{20})$) of the concentration of the surfactant in the bulk phase necessary to produce a 20 mN m^{-1} reduction in the surface tension of the solvent.

Surface pressure, $\Pi_{\mathrm{CMC},}$ is calculated by the difference between the value of the surface tension of the water, γ_w, and that of the surfactant solution at the CMC, γ_{CMC}, according to the following relation:

$$\Pi_{CMC} = \gamma_w - \gamma_{CMC}. \tag{9}$$

The standard free energy of adsorption was calculated using to Eq. 10:

$$\Delta G_{ad}^0 = (2-\alpha)\mathrm{R}TLn\left(\frac{\mathrm{CMC}}{\omega}\right) - \frac{\Pi}{\Gamma_m} \tag{10}$$

The critical packing parameter of surfactants, CPP, whose value corresponds to the morphology of the aggregate, is defined as:

$$\mathrm{CPP} = \frac{V_H}{a_0 \times l_C} \tag{11}$$

where V_H is the effective volume of the hydrophobic chains, where a_0 is the surface of the polar head and l_C is the length of the alkyl chain. At saturation, a_0 can be replaced by $A_{\min}$.

The volume, V_H, of a hydrophobic chain depends on the number of carbon atoms, n, inserted in the hydrophobic core (Myers, 1999; Tanford, 1980):

$$V_H = 27.4 + 26.9 \times (n-1) \quad \mathring{A}^3 \tag{12}$$

the length of the hydrophobic chain I_C can also be estimated according to n:

$$l_C \leq 1.5 + 1.265 \times (n-1) \quad \mathring{A}. \tag{13}$$

For the aggregation number, N, although it was hard and complex to use conventional methods such as ^{1}H NMR measurement and fluorescence quenching to obtain the value of N, Mandal and coworkers and others have determined the value of N using the above and other various

Table 2 Surface properties of surfactants at 298,15 K: Critical micellar concentration (CMC), surface tension of the CMC (γ CMC), surface excess concentration Γ_m, minimum area per molecule ($A_{\min}$), efficiency pC_{20}, the surface pressure Π, critical packing parameter CPP, free energy of adsorption ΔG^0_{ad}, and the aggregation number N

Surface properties	C_{12}PrOH	C_{12}EtOH	C_{12}iPrOH	C_{14}PrOH	C_{14}EtOH	C_{14}iPrOH
CMC (mmol L^{-1})	25	15	11.7	2.13	1.77	1.47
γ_{CMC} (mN m^{-1})	33.9	33.9	35.2	33.5	33.1	35.1
Π(mN m^{-1})	39.1	39.2	37.8	39.6	40	37.9
pC_{20}	2.7	3.3	3.5	3.9	4.3	4.6
Γ_m(mol cm^{-2})	1.42×10^{-10}	1.07×10^{-10}	9.87×10^{-11}	1.40×10^{-10}	1.00×10^{-10}	8.83×10^{-11}
A (Å^2)	116.54	155.07	168.19	118.51	164.92	188.05
CPP	0.18	0.13	0.12	0.17	0.12	0.11
ΔG^0_{ad}(kJ mol^{-1})	−55.92	−67.75	−70.85	−70.33	−82.82	−87.59
Aggregation number N	25	19	17	34	24	21

techniques (Bossev et al., 1999; James et al., 2005; James and Mandal, 2011a, 2011b; Krishnan et al., 2003, 2004; Szajdzinska-Pietek and Wolszczak, 2000).

The value of N can be calculated according to the following equation (Wadekar et al., 2012):

$$N = \frac{4 \times \pi \times l_C^2}{A_{\min}} \tag{14}$$

All the results of surface tension properties and aggregation number are summarized in Table 2.

UV–Visible Spectroscopy Measurements

As can be seen from Tables 1 and 2, the CMC and the other physicochemical parameters of surfactants studied depend on the position of the OH group with respect to quaternary ammonium N^+, and the linear alkyl chain, for both C_{12} and C_{14} series.

To explain these effects, we have used the sensitivity of OM dye when it is complexed with a cationic surfactant (Akbaş and Kartal, 2007; Mishra and Haram, 2004). This study leads to understand the relation between the degree of ionization, α, the value of CMC, and the degree of hydration of micelles, this relation can be followed by the displacement of the maximum absorption wavelength, $\lambda_{\max}$, of the OM solutions at different concentrations of the surfactant.

Figure 3 shows a typical form of the variation of absorbance of OM in the absence and in the presence of surfactant below and above the CMC. The concentration of OM retained to conduct this work is 50 μmol L^{-1} that gives the suitable absorbance value (Alehyen et al., 2010). The band at 465 nm corresponds to the solution of OM in the absence of surfactants according to Rinuy et al. (2000), this band is attributed to the π—π* transition of the hydrated form of OM. On the other hand, Giri et al. (2012) assign the same band to a $n \rightarrow \pi^*$ transition. The band 431 nm corresponds to the detection of the surfactant micelles in the case of C_{14}PrOH. The results obtained for the other surfactants for this band are summarized in Table 3. The 377 nm band has been observed for many surfactant and cationic polymer systems, and its origin has been a subject of debates (Buwalda and Engberts, 2001).

Figure 4 shows the normalized absorbance spectra obtained for OM alone (50 μmol L^{-1}) and the solutions of surfactant concentration higher than the CMC (8 mmol L^{-1}) for C_{14}PrOH, C_{14}EtOH, and C_{14}iPrOH. We observe an offset of the spectra of OM as a function of the OH location, between 423 nm and 429 nm for the C_{14} series and from 429 to 433 nm for the C_{12} series. The value of $\Delta\lambda_{\max}$ increases while CMC and α values decrease.

Discussion

If the effect of hydrocarbon length on the variation of the CMC is well known (Klevens, 1953; Rosen et al., 1999), it

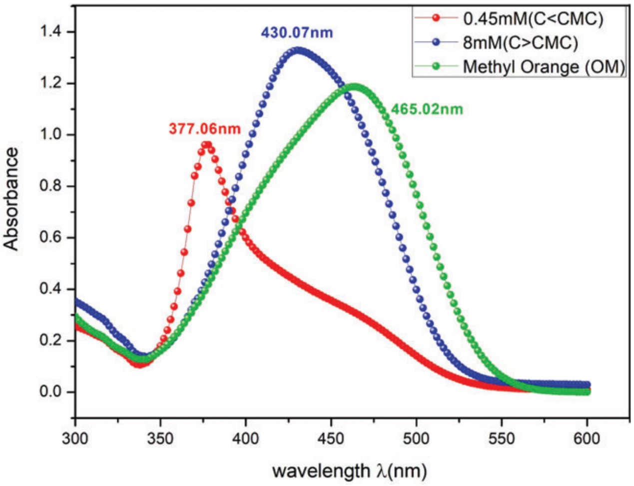


Fig. 3 UV–Vis absorption spectrum of Methyl orange OM at different concentrations of the C_{14}PrOH (0.45 and 8 mmol) surfactant at 298.15 K and neutral pH

Table 3 Variation of the maximum wavelength λ_{max} of surfactants at 298.15 K, neutral pH, and surfactant concentration C > CMC

Surfactants	C_{12}PrOH	C_{12}EtOH	C_{12}iPrOH	C_{14}PrOH	C_{14}EtOH	C_{14}iPrOH
wavelength λ_{max}	432.77 nm	430.07 nm	429.05 nm	428.67 nm	426.80 nm	423.20 nm

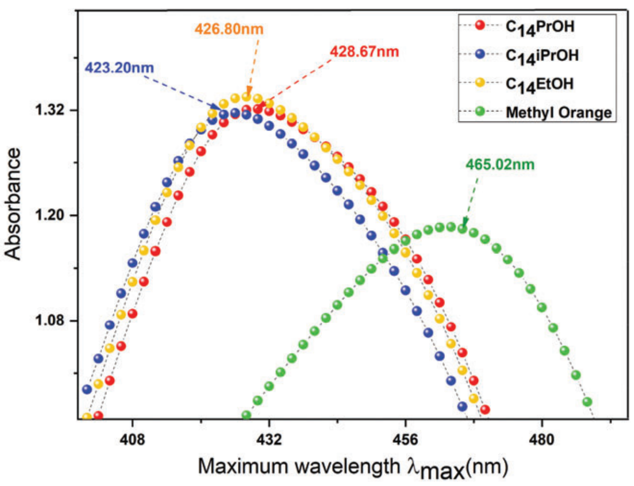


Fig. 4 UV–Vis absorption spectrum of methyl orange (OM) at the highest concentration of CMC (8 mmol) for the surfactants of C_{14}PrOH, C_{14}EtOH, and C_{14}iPrOH at 298.15 K and neutral pH

is not the same for the variations of the physicochemical parameters accompanying the micellization. Also the effect of the polar head is often not very well studied and the results of the literature in this area remain scattered (Chevalier et al., 1991; Dahanayake and Rosen, 1984; Hajji et al., 1990; Omar and Abdel-Khalek, 1998; Venable and Nauman, 1964).

The examination of the polar head of our studied products suggests the presence of two polar parts, the ammonium group and the hydroxyl group. The discussion of this article will be devoted to these two factors: the increase of the linear hydrophobic carbon chain and the location of the alcohol function with respect to the quaternary ammonium.

Effect of Hydrocarbon Chain

As can be seen from Tables 1 and 2, the CMC values of the surfactants obtained using both conductometric and surface tension measurements decrease as a function of the increase of the linear alkyl chain. The increase of the hydrophobic chain by two methylene-groups, —$(CH_2)_2$—, leads to a decrease in the CMC following the Klevens equation (Klevens, 1953; Rosen et al., 1999).

$$\log(\mathrm{CMC}) = A - Bm \tag{15}$$

Parameters *A* and *B* are known as Klevens constants, and are available in the literature for many surfactants (Rosen and Kunjappu, 2012) and m is the number of carbon atoms in the hydrophobic chains.

We must note that the CMC values reported in Tables 1 and 2 are very different: those obtained from conductivity measurements are more precise (linear scale, instead of logarithmic for surface tension). From the measurement of the surface tension, we note that the maximum surface excess Γ_m decreases slightly as the hydrophobicity of the surfactant molecules increases. Indeed, according to Table 2 when the hydrophobic chain length is incremented by two methylenes —$(CH_2)_2$—, Γ_m decreases slightly, therefore the value of the occupied area at the interface, $A_{\min}$, increases, this means a rapid saturation of the interface. This result can also confirm the value of CMC, which decreases from C_{12} to C_{14} for the three types of molecules studied. These results are in agreement with those of Venable and Nauman (1964), who found that for quaternary ammonium surfactants, the increase in the length of the alkyl chain leads to an increase of $A_{\min}$ and a decrease of Γ_m.

From geometrical considerations, (Eq. 14) the number of aggregation, N, of the micelles should increase with an increase of the hydrophobic part l_C of the surfactant molecule, and decrease with the increase of the occupied area of the molecule at the interface, $A_{\min}$.

In fact, Table 2 shows N increases from 12 to 14 carbon atoms (l_C increases), which is in agreement with the results obtained by Lianos and Zana (1981) for the cationic surfactants: decyl-, dodecyl-, tetradecyl-, and hexadecyl trimethyl ammonium bromides (DTAB, DDTAB, TTAB, and HDTAB, respectively): they find that *N* increases with the increase of the alkyl chain from 10 to 16 carbon atoms (from DTAB to HDTAB).

For the other physicochemical parameters calculated, such as Π_{CMC}, pC_{20}, and $\Delta G^0_{M,\mathrm{ad}}$, it is clearly observed that Π_{CMC} and pC_{20} increase as a function of the hydrophobicity of the molecule. The adsorption efficiency pC_{20} is correlated with the hydrophobicity of the most surfactants (Romsted, 2014).

The values of the free energies of adsorption at the air/-water interface, ΔG^0_{ad}, and micellization in aqueous media, ΔG^0_M, are negative and confirm that the spontaneous processes of adsorption and micellization are made easier with hydrophobic chain lengthening.

Effect of Polar Head

The results reported in this work clearly show that the position of the OH group in the polar head with respect to quaternary ammonium, N^+, affects the physicochemical parameters accompanying micellization and adsorption. For the two-examined series, C_{12} and C_{14}, the CMC obtained by conductometric and surface tension measurements decrease in the following order C_nPrOH > C_nEtOH > C_niPrOH.

The maximum surface excess Γ_m and minimum area per molecule $A_{\min}$ are well affected by the position of OH. It was found that the surface area occupied by the molecule at the interface has the largest value for C_niPrOH, followed by C_nEtOH and C_nPrOH.

It should be noted that the addition of two methylenes —$(CH_2)_2$— between two polar groups N^+ and OH causes a decrease of $A_{\min}$, from C_{12}EtOH to C_{14}PrOH. This result is in disagreement with Rosen and Kunjappu (2012), which indicates that if the hydrophobic part of the molecule lies between two polar groups, it tends to lie flat in the interface and that the surface occupied by the molecule in the interface is increased, this is proved also by the work of Chevalier et al. (1991).

The position of the OH group with respect to N^+ also has a significant effect on the values of *N*: according to Table 2, it is clearly remarkable that the increase of $A_{\min}$ decreases the value of *N* for both C_{12} and C_{14} series. The same behavior was observed Lianos and Zana (1982), for tetradecyltrialkylammonium bromides ($C_{14}H_{29}N^+(C_mH_{2m+1})_3Br^-$). They found that, in micellar solutions, *N* decreases with increasing size of the head group from 1 to 4 carbon atoms.

For the other parameters, pC_{20}, Π_{CMC}, and ΔG_M^0 and ΔG_{ad}^0, the variation of the position of OH with respect to N^+ does not have the same behavior as the effect of hydrophobicity on Π_{CMC}, such that the latter varies in the opposite order of the CMC, but the same variation of the pC_{20} behavior the effect of hydrophobicity with respect to CMC was observed for the effect of the location of OH with respect to N^+ according to the following order C_nPrOH > C_nEtOH > C_niPrOH.

The micellization and adsorption free energies, ΔG_M^0 and ΔG_{ad}^0, were all negative, confirming the spontaneity of formation of micelles and adsorption. As a function of CMC and $A_{\min}$, which shows that with each transition from C_nPrOH to C_nEtOH, C_nPrOH to C_niPrOH, and C_nEtOH to C_niPrOH, the CMC and $A_{\min}$ values indicate spontaneous adsorption and formation of micelles.

According to the theory of the micellar structure developed by Israelachvili et al. (1977) and Mitchell and Ninham (1981), the values of CPP are all in the range of $0 \le \text{CPP} \le \frac{1}{3}$, which corresponds to spherical micelles.

From the above discussion, it was found that the position of the OH group and the alkyl chain length affect all parameters accompanying the micellization phenomena. To understand this phenomenon better, we have used the interaction of surfactants with the OM dye. The sensitivity of an anionic dye to the presence of a cationic surfactant allows us to use the variation of its maximum absorption wavelength, $\lambda_{\max}$, when it is complexed with surfactant (Karukstis et al., 1998). This study leads to give an idea about the relationship between the degree of hydration of micelles and their degree of ionization, α.

As can be seen from Table 3, $\Delta\lambda_{\max}$ varies in the following order C_nPrOH > C_nEtOH > C_niPrOH in the same order of CMC. This result is also consistent with those obtained for the degree of ionization α that increases in the same order, the same behavior is also observed for surfactants 2-(decyldimethylammonio) alkanol bromides, such that the passage from 2-decyldimethylammoniobutannol bromides to 2-decyldimethylammonoethanol bromide shows that the two magnitudes CMC and α vary in the same order (Hajji et al., 1990). The degree of ionization expresses in fact the degree of hydration of the micelles, according to Soldi et al. (2000).

According to Muller et al. (1972), the first methylene groups of the hydrophobic chain adjacent to the hydrophilic head are often considered in the sphere of hydration. It is, therefore, useful to divide the interior region of the micelle into an outer sphere that can be penetrated by water and an internal one from which water is excluded.

We can then say that the higher the degree of ionization, the higher the rate of penetration of water molecules into the hydration sphere, which also leads to an increase in the proportion of OM hydrated between the hydrophobic chains of the surfactant (Akram et al., 2014), which itself leads to an increase in the maximum wavelength, $\lambda_{\max}$, according to Fig. 4. According to this agreement, we can conclude that is a correlation between the three parameters CMC, α, and $\lambda_{\max}$ as indicated in Fig. 5.

Conclusion

Cationic surfactants in the series of N-(hydroxyalkyl)-N,N-dimethyl n-alkylammonium bromides with various alkyl chain lengths and various hydrophilic groups were synthesized from amino alcohols and alkyl bromides and characterized using the usual spectroscopic methods (^{1}H, ^{13}C NMR and IR), their physicochemical properties were calculated using conductivity, surface tension, and UV spectroscopic measurements.

The effects of the hydrophobicity of the alkyl chain and the polar part on the variation of the physicochemical parameters accompanying the micellization and adsorption were discussed.

The effect OH with respect to N^+ on the property of micellization and adsorption was clearly studied. The intermolecular interaction approach between the synthetic

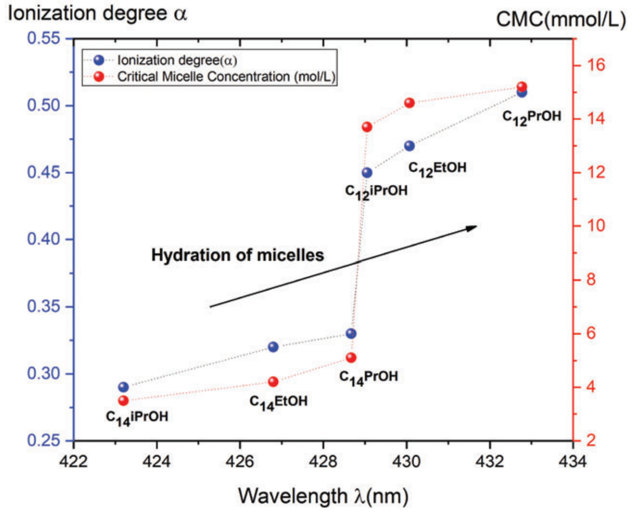


Fig. 5 Correlation between the degree of ionization α, CMC critical micelle concentration. and maximum wavelength $\lambda_{\max}$ for the three types of surfactants C_nPrOH, C_nEtOH, and C_niPrOH (n = 12 and 14) for both C_{12} and C_{14} series

surfactants and the OM dye was performed to understand the relationship between the degree of hydration and the degree of ionization α of the micelles.

The results show that the value of CMC, the degree of ionization, α, and the degree of hydration of the micelle related to the hypsochromic displacement of OM wavelength, $\lambda_{\max}$, follow the same trend.

Conflict of Interest The authors declare that they have no conflict of interest.

References

Akbaş, H., & Kartal, Ç. (2007) Conductometric studies of the interaction of C.I. Reactive orange 16 with cationic alkyltrimethylammonium bromide surfactants. *Dyes and Pigments*, **72**:383–386.

Akram, M., Bhat, I. A., & Kabir-Ud-Din (2015) Self-aggregation of surfactant ethane-1,2-diyl bis(N, N -dimethyl- N -hexadecylammoniumacetoxy) dichloride: Tensiometric, microscopic, and spectroscopic studies. *Journal of Physical Chemistry B*, **119**:3499–3509.

Akram, M., Yousuf, S., Sarwar, T., & Kabir-ud-Din (2014) Micellization and interfacial behavior of 16-E2-16 in presence of inorganic and organic salt counterions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **441**:281–290.

Alehyen, S., Bensejjay, F., El Achouri, M., Pérez, L., & Infante, M. R. (2010) Study of the interaction between methyl orange and mono and bis-quaternary ammonium surfactants. *Journal of Surfactants and Detergents*, **13**:225–231.

Bossev, D. P., Matsumoto, M., & Nakahara, M. (1999) ^{1}H and ^{19}F NMR study of the counterion effect on the micellar structures formed by tetraethylammonium and lithium perfluorooctylsulfonates. 1. Neat systems. *The Journal of Physical Chemistry B*, **103**: 8251–8258.

Buwalda, R. T., & Engberts, J. B. F. N. (2001) Aggregation of dicationic surfactants with methyl orange in aqueous solution. *Langmuir*, **17**:1054–1059.

Chevalier, Y., Storet, Y., Pourchet, S., & Le Perchec, P. (1991) Tensioactive properties of zwitterionic carboxybetaine amphiphiles. *Langmuir*, **7**:848–853.

Dahanayake, M., & Rosen, M. J. (1984) Surface properties of zwitterionic surfactants 1. Synthesis and properties of some betaines and sulfobetaines. In *ACS Symposium Series* (Vol. 253, Chapter 3, pp. 49–59). Washington, DC: American Chemical Society.

Giri, M., Singh, D., Lal, J., Jaggi, N., Singh, N., & Prasad Jaiswal, R. M. (2012) Atti Della "Fondazione Giorgio Ronchi". *LXVII*, **2**:3–9.

Gotmukle, S. B., & Bhagwat, S. S. (2013) Synthesis and surface activity of bisphosphate gemini surfactants. *Journal of Surfactants and Detergents*, **16**:63–70.

Grillo, I., Penfold, J., Tucker, I., & Cousin, F. (2009) Spontaneous formation of nanovesicles in mixtures of nonionic and dialkyl chain cationic surfactants studied by surface tension and SANS. *Langmuir*, **25**:3932–3943.

Hajji, S. M., Azize, B., Cao, A., Coudert, R., Hantz, E., Durand, R. R., & Taillandier, E. (1990) Effect of the polar head in the micellization of 2-(decyldimethylammonio)alkanol bromides in aqueous solutions. *Journal of Physical Chemistry*, **94**:7220–7224.

Holmberg, K. (2002) *Handbook of applied surface and colloid chemistry* (Vol. **1**). Chichester, England: John Wiley & Sons LTD.

Israelachvili, J. N., Mitchell, D. J., & Ninham, B. W. (1977) Theory of self-assembly of lipid bilayers and vesicles. *Biochimica et Biophysica Acta*, **470**:185–201.

James, J., & Mandal, A. B. (2011a) Micelle formation of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solution and their influence on the aggregation of SDS and PEO-PPO-PEO copolymer micelles. *Colloids and Surfaces B: Biointerfaces*, **84**:172–180.

James, J., & Mandal, A. B. (2011b) The aggregation of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solution and in the presence of SDS and PEO-PPO-PEO triblock copolymer: Fluorescence spectroscopic studies. *Journal of Colloid and Interface Science*, **360**:600–605.

James, J., Vellaichami, S., Krishnan, R. S. G., Samikannu, S., & Mandal, A. B. (2005) Interaction of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymer of molecular weight 2800 with sodium dodecylsulfate (SDS) micelles: Some physicochemical studies. *Chemical Physics*, **312**:275–287.

Kabir-ud-Din, Fatma, W., Khatoon, S., Khan, Z. A., & Naqvi, A. Z. (2008) Surface and solution properties of alkanediyl-α,ω-bis (dimethylcetylammonium bromide) Gemini surfactants in the presence of additives. *Journal of Chemical & Engineering Data*, **53**: 2291–2300.

Karukstis, K. K., Savin, D. A., Loftus, C. T., & D'Angelo, N. D. (1998) Spectroscopic studies of the interaction of methyl orange with cationic alkyltrimethylammonium bromide surfactants. *Journal of Colloid and Interface Science*, **203**:157–163.

Klevens, H. B. (1953) Structure and aggregation in dilute solution of surface active agents. *Journal of the American Oil Chemists Society*, **30**:74–80.

Krishnan, R. S. G., Thennarasu, S., & Mandal, A. B. (2003) Self-assembling characteristics of 5-(α-acetamido-α-benzyl) methyl-5′-methyl imidazolidine-2,4-dione—A hydantoin drug. *Chemical Physics*, **291**:195–205.

Krishnan, R. S. G., Thennarasu, S., & Mandal, A. B. (2004) Self-assembling characteristics of a new nonionic gemini surfactant. *Journal of Physical Chemistry B*, **108**:8806–8816.

Lianos, P., & Zana, R. (1981) Fluorescence probe studies of the effect of concentration on the state of aggregation of surfactants in aqueous solution. *Journal of Colloid and Interface Science*, **84**: 100–107.

Lianos, P., & Zana, R. (1982) Micelles of tetradecyltrialkylammonium bromides with fluorescent probes. *Journal of Colloid and Interface Science*, **88**:594–598.

Lv, J., Qiao, W., & Xiong, C. (2014) Synthesis and surface properties of a pH-regulated and pH-reversible anionic Gemini surfactant. *Langmuir*, **30**:8258–8267.

Maiti, K., Mitra, D., Guha, S., & Moulik, S. P. (2009) Salt effect on self-aggregation of sodium dodecylsulfate (SDS) and tetradecyltrimethylammonium bromide (TTAB): Physicochemical correlation and assessment in the light of Hofmeister (lyotropic) effect. *Journal of Molecular Liquids*, **146**:44–51.

Migahed, M. A., Negm, N. A., Shaban, M. M., Ali, T. A., & Fadda, A. A. (2016) Synthesis, characterization, surface and biological activity of diquaternary cationic surfactants containing ester linkage. *Journal of Surfactants and Detergents*, **19**:119–128.

Mishra, A., & Haram, N. S. (2004) New push-pull type dendritic stilbazolium dyes: Synthesis, photophysical and electrochemical investigation. *Dyes and Pigments*, **63**:191–202.

Mitchell, D. J., & Ninham, B. W. (1981) Micelles, vesicles and microemulsions. *Journal of the Chemical Society, Faraday Transactions 2*, **77**:601–629.

Moreira, L. A., & Firoozabadi, A. (2009) Thermodynamic modeling of the duality of linear 1-alcohols as cosurfactants and cosolvents in self-assembly of surfactant molecules. *Langmuir*, **25**:12101–12113.

Muller, N., Pellerin, J. H., & Chen, W. W. (1972) Investigation of micelle structure by fluorine magnetic resonance.VI Quaternary ammonium salts. *The Journal of Physical Chemistry*, **76**: 3012–3017.

Myers, D. (1999) *Surfaces, interfaces and colloids: Principles and applications* (2nd ed.). Hoboken, NJ: John Wiley & Sons, Inc.

Nakagaki, M., & Handa, T. (1984) Effect of structure on activity at the critical micelle concentration and on the free energy of micelle formation. In *ACS Symposium Series* (Vol. 253, Chapter 5, pp 73–86). Washington, DC: American Chemical Society.

Nilsson, M., Valente, A. J. M., Olofsson, G., Soderman, O., & Bonini, M. (2008) Thermodynamic and kinetic characterization of host-guest association between bolaform surfactants and α- and β-cyclodextrins. *The Journal of Physical Chemistry. B*, **112**: 11310–11316.

Omar, A. A. M. A., & Abdel-Khalek, N. A. (1998) Surface and thermodynamic parameters of some cationic surfactants. *Journal of Chemical and Engineering Data*, **43**:117–120.

Pan, A., Naskar, B., Prameela, G. K. S., Kumar, B. V. N. P., Mandal, A. B., Bhattacharya, S. C., & Moulik, S. P. (2012) Amphiphile behavior in mixed solvent media I: Self-aggregation and ion association of sodium dodecylsulfate in 1,4-dioxane-water and methanol-water media. *Langmuir*, **28**:13830–13843.

Phani Kumar, B. V. N., Reddy, R. R., Pan, A., Aswal, V. K., Tsuchiya, K., Prameela, G. K. S., … Moulik, S. P. (2018) Physicochemical understanding of self-aggregation and microstructure of a surface-active ionic liquid [C_4mim] [C_8OSO_3] mixed with a reverse pluronic 10R5 ($PO_8EO_{22}PO_8$). *ACS Omega*, **3**:5155–5164.

Phani Kumar, B. V. N., Umayal Priyadharsini, S., Prameela, G. K. S., & Mandal, A. B. (2011) NMR investigations of self-aggregation characteristics of SDS in a model assembled triblock copolymer solution. *Journal of Colloid and Interface Science*, **360**:154–162.

Prameela, G. K. S., Phani Kumar, B. V. N., Aswal, V. K., & Mandal, A. B. (2013) Influence of water-insoluble nonionic copolymer $E_6P_{39}E_6$ on the microstructure and self-aggregation dynamics of aqueous SDS solution—NMR and SANS investigations. *Physical Chemistry Chemical Physics*, **15**:17577–17586.

Prameela, G. K. S., Phani Kumar, B. V. N., Pan, A., Aswal, V. K., Subramanian, J., Mandal, A. B., & Moulik, S. P. (2015) Physicochemical perspectives (aggregation, structure and dynamics) of interaction between pluronic (L31) and surfactant (SDS). *Physical Chemistry Chemical Physics*, **17**:30560–30569.

Prameela, G. K. S., Phani Kumar, B. V. N., Reddy, R. R., Pan, A., Subramanian, J., Kumar, S., … Moulik, S. P. (2017) Vesicle to micelle transition in the ternary mixture of L121/SDS/D_2O: NMR, EPR and SANS studies. *Physical Chemistry Chemical Physics*, **19**: 31747–31755.

Rinuy, J., Piron, A., Brevet, F. P., Blanchard-desce, M., & Girault, H. H. (2000) Intramolecular electron density redistribution upon hydrogen bond formation in the anion methyl orange at the water/1,2-dichloroethane interface probed by phase interference second harmonic generation. *Chemistry - A European Journal*, **6**: 3434–3441.

Romsted, L. S. (2014), *Surfactant science and technology: Retrospects and prospects*. Boca Raton, FL: Taylor & Francis Group.

Rosen, M. J., & Kunjappu, J. T. (2012) *Surfactants and phenomena* (4th ed.). Hoboken, NJ: John Wiley & Sons, Inc.

Rosen, M. J., Mathias, J. H., & Davenport, L. (1999) Aberrant aggregation behavior in cationic Gemini surfactants investigated by surface tension, interfacial tension, and fluorescence methods. *Langmuir*, **15**:7340–7346.

Shah, S. K., Chatterjee, S. K., & Bhattarai, A. (2016) The effect of methanol on the micellar properties of dodecyltrimethylammonium bromide (DTAB) in aqueous medium at different temperatures. *Journal of Surfactants and Detergents*, **19**:201–207.

Soldi, V., Keiper, J., Romsted, L. S., Cuccovia, I. M., & Chaimovich, H. (2000) Arenediazonium salts: New probes of the interfacial compositions of association colloids. 6. Relationships between interfacial counterion and water concentrations and surfactant headgroup size, sphere-to-rod transitions, and chemical reactivity in cationi. *Langmuir*, **16**:59–71.

Szajdzinska-Pietek, E., & Wolszczak, M. (2000) Time-resolved fluorescence quenching study of aqueous solutions of perfluorinated surfactants with the use of protiated luminophore and quencher. *Langmuir*, **16**:1675–1680.

Tanford, C. (1980) *The hydrophobic effect: Formation of micelles and biological membranes* (2nd ed.). New York, NY: Wiley-Interscience.

Venable, R. L., & Nauman, R. V. (1964) Micellar weights of and solubilization of benzene by a series of tetradecylammonium bromides. The effect of the size of the charged head. *The Journal of Physical Chemistry*, **68**:3498–3503.

Wadekar, M. N., Boekhoven, J., Jager, W. F., Koper, G. J. M., & Picken, S. J. (2012) Micellization behavior of aromatic moiety bearing hybrid fluorocarbon sulfonate surfactants. *Langmuir*, **28**: 3397–3402.

Wattebled, L., & Laschewsky, A. (2007) Effects of organic salt additives on the behavior of dimeric ('Gemini') surfactants in aqueous solution. *Langmuir*, **23**:10044–10052.

Zana, R. (1996) Critical micellization concentration of surfactants in aqueous solution and free energy of micellization. *Langmuir*, **12**: 1208–1211.