

Experimental and Theoretical Approach to Nonequivalent Adsorption of Novel Dicephalic Ammonium Surfactants at the Air/Solution Interface

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The interfacial behavior of novel dicephalic cationic surfactants, *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dibromides and *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dimethylsulfates, was analyzed both experimentally and theoretically in comparison to their linear standards, 3-[(trimethylammonio)propyl]dodecanamide bromide and 3-[(trimethylammonio)propyl]dodecanamide methylsulfate. Adsorption of the studied double head–single tail surfactants depends strongly upon their structure, making them less surface active in comparison to the single head–single tail structures having the same alkyl chain length. Surface tension isotherms of aqueous solutions of the studied dicephalic derivatives were measured using the pendant drop shape analysis method and interpreted with the so-called surface quasi-two-dimensional electrolyte (STDE) model of ionic surfactant adsorption. The model is based on the assumption that the surfactant ions and counterions (bromide and methylsulfate ions in the studied case) undergo nonequivalent adsorption within the Stern layer, and it allows for accounting for the formation of surfactant ion–counterion associates in the case of multivalent surfactant headgroup ions. As a result, good agreement between theory and experiment was obtained. Additionally, the presence of surfactant–counterion complexes was successfully confirmed by both measurements of the concentration of free bromide ions in solution and molecular modeling simulations. The results of the present study may prove useful in the potential application of the investigated dicephalic cationic surfactants.

I. Introduction

New cationic surfactants are continuously being designed and synthesized in order to attain products with specific physico-chemical properties for targeted applications.^{1–4} The key issues in surfactant-based formulations are the structure–performance relationships and the chemical compatibility; therefore, much research is being devoted to these areas. Even slight modifications of the molecular structure with respect to the conventional single head–single tail design of cationic structures allow for a variety of possible applications.^{5–7} Such a modulation enables one to obtain variously organized systems by incorporation of the additional alkyl chain or polar group into the surfactant molecule. This may lead to double tail–single head surfactants,⁸ multihead–single tail structures,⁹ bola-type,¹⁰ gemini (or dimeric), and oligomeric representatives.^{11–15}

Among many known ionic surfactants, functionalized quaternary ammonium salts form a large group of currently used or studied compounds and their popularity keeps growing.^{1,9,11,12,15,16} Many cationic substances^{17–19} (and references therein) have found uses as antiseptic agents, fungicides, antistatic substances, as well as catalysts in various syntheses of new chemicals, and have been used or proposed for use in the pharmaceutical, cosmetic, textile, paint, and coating industries as emulsifying agents, suspension stabilizers, and wetting and foaming agents. Much attention has recently been focused on their solubilization properties and on their use as delivery agents and templates for a variety of nanostructures, new drug components, models for

biomembranes, or reaction media.^{4,20} A relatively large number of cationic surfactants has been investigated in recent years, the vast majority of reports dealing with description of the relationships between the chemical structure of the surfactant and the nature and properties of the concentrated surfactant monolayer at the interfaces.^{12,21–26} Due to their structural features, these surfactants exhibit a unique behavior for self-organization at the interface or in bulk solutions.

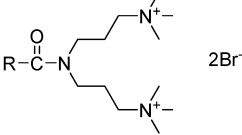
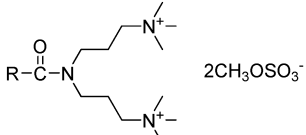
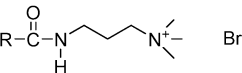
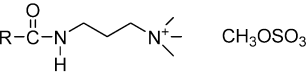
As a continuation of our studies on adsorption and aggregation phenomena of new functionalized cationic surfactants,^{11,16,25–28} we present here our contribution dealing with two newly synthesized homologous series of dicephalic type amphiphilic molecules: *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dibromides and *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dimethylsulfates along with, for comparison, linear 3-[(trimethylammonio)propyl]dodecanamide bromide and 3-[(trimethylammonio)propyl]dodecanamide methylsulfate whose formulas are shown (together with their abbreviations) in Chart 1. Double head–single tail structures have been mostly studied for nonionics (commercialized examples are oxyethylenated primary amines, oxyethylenated amides, alkyliminodipropionic acids and their salts, and many others), but the term dicephalic surfactants was developed by Sommerdijk et al.²⁹ for amphiphilic derivatives of imidazole and phosphoric acid, whose aggregates are able to complex metal ions. The present contribution reports new and original experimental and theoretical basic research concerning adsorption of new functionalized bis-ammonium (so-called dicephalic or double-headed) derivatives which belong to a large group of currently used or studied compounds and whose popularity keeps growing nowadays. To the best of our knowledge, there have been no reports so far on the adsorption properties (considered both experimentally and

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CHART 1: Structural Formulas of Bis-ammonium Dibromides $C_n(\text{TAPABr})_2$, Bis-ammonium Dimethylsulfates $C_n(\text{TAPAMS})_2$, Single Head–Single Tail Bromide $C_{12}\text{TAPABr}$, and Single Head–Single Tail Methylsulfate $C_{12}\text{TAPAMS}$

Structure	R	Abbreviation
 N,N -bis[3,3'-(trimethylammonio)propyl]alkylamide dibromides	C_9H_{19}	$C_{10}(\text{TAPABr})_2$
	$C_{11}H_{23}$	$C_{12}(\text{TAPABr})_2$
	$C_{13}H_{27}$	$C_{14}(\text{TAPABr})_2$
	$C_{15}H_{31}$	$C_{16}(\text{TAPABr})_2$
 N,N -bis[3,3'-(trimethylammonio)propyl]alkylamide dimethylsulfates	C_9H_{19}	$C_{10}(\text{TAPAMS})_2$
	$C_{11}H_{23}$	$C_{12}(\text{TAPAMS})_2$
	$C_{13}H_{27}$	$C_{14}(\text{TAPAMS})_2$
	$C_{15}H_{31}$	$C_{16}(\text{TAPAMS})_2$
 3-[(trimethylammonio)propyl]dodecanamide bromide	$C_{11}H_{23}$	$C_{12}\text{TAPABr}$
 3-[(trimethylammonio)propyl]dodecanamide methylsulfate	$C_{11}H_{23}$	$C_{12}\text{TAPAMS}$

theoretically) and characteristics of the surfactant monolayer of any dicephalic cationic surfactants. The adsorption of the designed dicephalic dibromides and dimethylsulfates at the air/solution interface and its theoretical description in terms of the advanced model of multicharge surfactant adsorption, taking into account counterion specificity and formation of surfactant–counterion associates, is of major importance. The results of the present study may prove useful in the understanding of the adsorption layer nature of multicharge structures in view of their potential application in colloid and surface chemistry.

Experimental methods generally give the overall information of the surfactant adsorption, but the detailed data about the distribution of the ions in the diffuse layer can only be derived through the theoretical description of ionic surfactant adsorption. Explanation of the adsorption mechanism is of importance for a variety of practical phenomena; however, the theoretical description is complicated in the case of the ionic surfactants because of the multicomponent nature of such systems. The following entities are present: surfactant ions, counterions, and ions of salt added to control the ionic strength of the solution. The successful theoretical model should consider any electrical interactions between all ions, and furthermore, it should describe at least semiquantitatively the electric double layer (EDL) structure in such complex systems. In general, the theoretical models are based on the thermodynamics concept of the Gibbs dividing surface, in which the surface excess of any ionic compound is the total of its excesses in the actual monolayer and in the electrical double layer.^{30,31} Davies and Rideal³² and then Borwankar and Wasan³³ were the first who exploited the simple Gouy–Chapman model of the electrical double layer and assumed that the surfactant ions adsorb in the Stern layer and the counterions remain in the diffuse part of the electric double layer. By applying the Gibbs adsorption equation, they

obtained the dependence of the surface tension on the ionic surfactant concentration in solution. The thermodynamic model was proposed by Fainerman and Lucassen-Reynders.^{34,35} Those authors included the correction for activity coefficients of electrolyte solution and properly described the surface tension isotherms of selected cationic and anionic surfactants on the concentration of the added salt. However, they did not calculate surface potentials and did not consider ion specific effects. The model proposed by Kalinin and Radke³⁶ considered the counterion binding to surfactant ions adsorbed in the Stern layer. They adopted Grahame's³⁷ concept of the triple layer with counterions located at the plane different from that of the adsorbed surfactant head groups. That allowed for better agreement of calculated surface potentials with the experimentally observed ones. The adsorption of ionic surfactants was also theoretically considered by Kralchevsky et al.³⁸ For the experimental adsorption data description, we have developed so far the STDE (surface quasi-two-dimensional electrolyte) model of ionic surfactant adsorption which correctly describes the surface tension isotherms of anionic^{39,40} as well as some classical quaternary ammonium surfactants,²⁸ also in the presence of various electrolytes.^{25,26} Recently, taking into account the formation of surfactant ion–counterion complexes, we have successfully applied the model to the adsorption of dimeric and trimeric ammonium chloride surfactants at the air/solution interface.¹¹ Furthermore, the phenomenon of counterion condensation has already been predicted by Manning⁴¹ and a concept of counterion binding to dimeric surfactants has been used by Li et al.⁴² to reconcile the results obtained from surface tension measurements with those obtained by means of neutron reflectivity. Recently, the effect of counterion association was also taken into account in the evaluation of the colloidal stability and a generalized model for the colloidal stability was

proposed.^{43,44} The model accounts for the interplay among three physicochemical processes: colloidal interactions, surfactant adsorption equilibria, and association of equilibria of surface charge groups with counterions. The authors of the model demonstrated that DLVO theory can well describe the experimental results even at high electrolyte concentration, when the generalized model accounting for the counterion association is applied and for divalent ions it becomes even more important than for monovalent ions.

Model of Adsorption of Multiple Charge Surfactants. The main assumption of the STDE model of ionic surfactant adsorption is a statement that a strong electric field of surfactant ions adsorbed at the interface induces the “adsorption” of counterions within the interfacial Stern layer. The adsorbed ions keep their freedom of motion in that layer, which can be considered as a “surface quasi-two-dimensional electrolyte”, in which the electroneutrality condition is not fulfilled. The sum of the positive charge of the adsorbed surfactant headgroups and the negative charge of the counterions determines the total charge in the Stern layer, and furthermore the potential of the diffuse part of the electric double layer (EDL). The model takes explicitly into account both the finite size of the headgroups as well as the counterions, and lateral electric interactions between them. The basic assumptions given below remain applicable in the extension of the model to the description of the adsorption of multiple charge surfactants. However, these surfactants in the solution may not be fully dissociated, with partial association of the counterion to the dimeric or trimeric surfactant ion.^{11,45} As it was suggested in ref 15, the association should follow the mass action law, which in the case of multiple charge structures can be written in the form

$$K = \frac{c_{\text{surf}+2\text{counterion}}^{-1}}{c_{\text{surf}}+2c_{\text{counterion}}^{-1}} \quad (1)$$

where K is the association constant and c_i denotes the concentration of surfactant ions, counterions, and associates, respectively. Adsorption equations for the surfactant cations (including surfactant-counterion associates), their counterions, and anions of added electrolyte in the Stern layer can be formulated by exploiting the postulate of equilibrium, that is, by assuming equal electrochemical potentials of each ion for the bulk phase and in the Stern layer. Thus, the respective adsorption equations for the system of multivalent cationic surfactant ions with their counterions and anions of added electrolyte can be written as

$$\frac{a_S}{\alpha_S} \left(-\frac{z_S e \psi_s}{kT} \right) (1 - \theta_S - \theta_{SA} - \theta_{C1} - \theta_{C2}) = \theta_S \exp[-2H_S(\theta_S + \theta_{SA})] \exp\left(\frac{\phi_S}{kT}\right) \quad (2)$$

for surfactant cations (S),

$$\frac{a_{SA}}{\alpha_S} \left(-\frac{z_{SA} e \psi_s}{kT} \right) (1 - \theta_S - \theta_{SA} - \theta_{C1} - \theta_{C2}) = \theta_{SA} \exp[-2H_S(\theta_S + \theta_{SA})] \exp\left(\frac{\phi_S}{kT}\right) \quad (3)$$

for surfactant-counterion associates, and

$$\frac{a_{C1}}{\alpha_{C1}} \left(\frac{z_{C1} e \psi_s}{kT} \right) (1 - \theta_S - \theta_{C1} - \theta_{C2})^{g_{C1S}} = \theta_{C1} \exp\left(\frac{\phi_{C1}}{kT}\right) \quad (4)$$

$$\frac{a_{C2}}{\alpha_{C2}} \left(\frac{z_{C2} e \psi_s}{kT} \right) (1 - \theta_S - \theta_{C1} - \theta_{C2})^{g_{C2S}} = \theta_{C2} \exp\left(\frac{\phi_{C2}}{kT}\right) \quad (5)$$

for surfactant counterions (C1) and anions of added electrolyte (C2), respectively. Here, $a_i = \gamma_i c_i$ are the activities of surfactant ions, associates, and respective counterions in the solution, γ_i are activity coefficients, and c_i are concentrations. The activity coefficients can be calculated using the extended Debye-Hückel theory.⁴⁶ z_i are the respective valencies, α_S is the “surface activity” of the surfactant cation, being a measure of the free energy of the adsorption after separating the contribution of the electric components, and α_{C1} is the “surface activity” of the counterions, which is a measure of their penetration into the Stern layer due to van der Waals interactions, image forces, and hydration. For the multivalent ions, it also takes into account the correlation effects. $\theta_S = \Gamma_S/\Gamma_{S\infty}$, $\theta_{SA} = \Gamma_{SA}/\Gamma_{S\infty}$ is the relative surfactant and associate surface concentration, and $\Gamma_{S\infty}$ is the limiting surfactant surface concentration of a closely packed monolayer; $\theta_{C1} = \Gamma_{C1}/\Gamma_{C1\infty}$, $\theta_{C2} = \Gamma_{C2}/\Gamma_{C2\infty}$, and $\Gamma_{C1\infty}$ and $\Gamma_{C2\infty}$ are the same quantities for counterions, $g_{C1S} = \Gamma_{S\infty}/\Gamma_{C1\infty}$, $g_{C2S} = \Gamma_{S\infty}/\Gamma_{C2\infty}$, and H_S is the interaction parameter accounting for the attractive lateral interactions among the adsorbed surfactant hydrophobic tails. The electric potential of the Stern layer, Ψ_s , can be found from

$$\psi_s = \psi_d + \frac{\sigma \delta}{\epsilon_0 \epsilon_s} \quad (6)$$

If the multivalent ions are present in the solution, in contrast to a purely monovalent system, there is no analytical formula connecting the surface charge density:

$$\sigma = F(z_S \Gamma_S + z_{SA} \Gamma_{SA} + z_{C1} \Gamma_{C1} + z_{C2} \Gamma_{C2}) \quad (7)$$

and ψ_d is the diffuse layer potential at the boundary between the Stern layer and the diffuse part of the EDL, so it has to be calculated numerically using the implicit formula

$$\sigma = \left(\epsilon_0 \epsilon k T N_A \left(\sum_i c_i \left(\exp\left[-\frac{z_i e \psi_d}{kT}\right] - 1 \right) \right) \right)^{1/2} \quad (8)$$

where the contributions of all ionic species, that is, surfactant ions, their counterions, and ions of added electrolyte with respective valencies z_i , are included in the summation. Here, F and N_A are the Faraday constant and the Avogadro number, respectively, δ is the thickness of the Stern layer, and ϵ_s is the dielectric constant in the Stern layer. The activity corrections for the lateral interactions in a two-dimensional electrolyte φ_i can be calculated by means of the formula given in refs 25 and 40.

To calculate the total surface excess concentrations of all ionic species, the adsorption in the diffuse part of the EDL has to be considered. It can be found as

$$\Gamma_i^{\text{EDL}} = \frac{c_i}{\kappa} \int_0^{\psi_d} \frac{\exp\left[-\frac{z_i e \psi}{kT}\right] - 1}{s(\psi)} d\psi \quad (9)$$

where

$$s(\psi) = \left(\frac{2e^2 N_A}{\epsilon_0 \epsilon k T \kappa^2} \sum_i \left(c_i \exp\left[-\frac{z_i e \psi_d}{kT}\right] - 1 \right) \right)^{1/2}$$

and κ is the Debye–Hückel reciprocal length.

After the determination of the total surface excess concentrations of the surfactant ions and all other ions present in the solution, the surface tension can be calculated by integrating the Gibbs adsorption equation:

$$-d\gamma = \Gamma_{S^+}^T d\mu_{S^+} + \Gamma_{SA^+}^T d\mu_{SA^+} + \Gamma_{C1^-}^T d\mu_{C1^-} + \Gamma_{K^+}^T d\mu_{K^+} + \Gamma_{C2^-}^T d\mu_{C2^-} \quad (10)$$

where Γ^T 's are the total surface excess concentrations (including that in the diffuse part of the EDL, eq 10) for surfactant cations (S^+), surfactant–counterion associates (SA^+), surfactant counterions ($C1^-$, $C2^-$), and co-ions (K^+) and μ^T 's, $\mu_i = \mu_{i0} + RT \ln(a_i)$, are respective chemical potentials, where μ_{i0} is the standard chemical potential. For co-ions, only adsorption (negative) in the diffuse part of the EDL is considered. The quantitative approach, described above, gives a possibility to calculate surface tension isotherms as functions of surfactant concentration and to determine the surface (excess) concentrations of all species in the system as well as the electric potential of the electric double layer.

II. Materials and Methods

Experimental Section. The dicephalic *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dibromides (Cn(TAPABr)₂) and *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dimethylsulfates (Cn(TAPAMS)₂) were synthesized by the method described in ref 47. The linear ammonium surfactants 3-[(trimethylammonio)propyl]dodecanamide bromide (C₁₂TAPABr) and 3-[(trimethylammonio)propyl]dodecanamide methylsulfate (C₁₂TAPAMS) were synthesized by an analogous method as described in ref 47.

3,3'-Iminobis(*N,N*-dimethylpropylamine), dimethylaminopropylamine, dimethyl sulfate, and decanoyl, lauroyl, myristoyl, and palmitoyl chlorides were purchased from Aldrich Chemical Co. (Milwaukee, WI), and methyl bromide was purchased from Tedlee Chemical Corp. (Brooklyn, NY). Other reagents and solvents were of commercial grade and were not additionally purified before use. Water used for all experiments was doubly distilled and purified by means of a Millipore (Bedford, MA) Milli-Q purification system.

Surface Tension Measurements. The equilibrium surface tension measurements were performed using the pendant drop shape analysis method. The experimental setup for the equilibrium surface tension determination by this method is described in detail elsewhere.⁴⁸ The method is based on fitting the solution of the Young–Laplace equation of capillarity to the shape of the pendant drop, which is recorded by a digital camera. The measured surface tension value, being the only

unknown parameter in that equation, corresponds to the best-fit value. All surface tension measurements were performed at 295 K.

Bromide Activity Measurements. The bromide ion activity was measured with a pH/ionometer (Elmetron CP-501) with a bromide ion specific electrode (Hydromet type EBr-01) in conjunction with a Ag/AgCl reference electrode (Hydromet type RL-100). The calibration curve was obtained by measuring the electromotive force (EMF) of the KBr solutions in the concentration range 10^{−4}–10^{−1} M. Then, 50 mL samples of freshly prepared solutions of the investigated surfactants with added 1 mL of stabilizing solution were measured. The stabilizing solution was prepared by dissolving 425 g of NaNO₃ and 29 mL of CH₃COOH in 1 L of water. The equilibrium values of the EMF for dicephalic ammonium bromides were reached after 2–3 min, more slowly than those for KBr solutions. All measurements were performed at 22 °C.

Molecular Modeling. Molecular dynamics simulations of the formation of surfactant–counterion associates were performed using the HYPERCHEM 8.0 software package.⁴⁹ All calculations were performed using the AMBER 99⁵⁰ force field contained in the package. Partial atomic charges (ESP charges) needed for determination of the electrostatic interaction between surfactant cation and counterion were assigned according to the Merz–Singh–Kollman scheme⁵¹ applying the Gaussian 03 software⁵² for the surfactant structure optimized using Hartree–Fock computations with the 6-31G(d) basis set.

The molecular dynamic simulations were performed in the periodic box, whose dimensions corresponded to the mean distance between surfactant molecules at a given concentration. The Coulombic potential with the cutoff length of the size of the simulation box was used to calculate electrostatic interactions. The aqueous solvent was treated as a continuous dielectric medium with a dielectric constant of $\epsilon = 79$. The formula for the energy of electrostatic interactions was

$$E_e = \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 \epsilon r_{ij}} \quad (11)$$

where q_i is the ESP atomic charge of a given atom, ϵ_0 is the vacuum permittivity, and r_{ij} is the distance between interacting charges. To account for the effect of aqueous medium on the van der Waals interaction energy between nonbonded atoms, we scaled the attractive Lennard-Jones potential for the van der Waals attraction between the nonbonded atoms of the chain by a constant factor of 0.1.^{53–55} The computations were initiated by placing the surfactant ions and both counterions inside the simulation box with equilibration of the system at a constant temperature of 300 K. The molecular dynamic simulations were performed for 200 ns for a constant temperature of 300 K and using the Langevin dynamics approach with a friction coefficient of 30 ps^{−1} of aqueous solution. After the simulation run, the probability of surfactant–counterion association was calculated as the ratio of time when the system was in the associated state to the total simulation time. The final result was obtained as an average of five simulation runs.

III. Results and Discussion

The studied double charge (so-called dicephalic or double-headed) *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dibromides Cn(TAPABr)₂ and *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dimethylsulfates Cn(TAPAMS) are attracting particular interest because their synthesis is relatively straight-

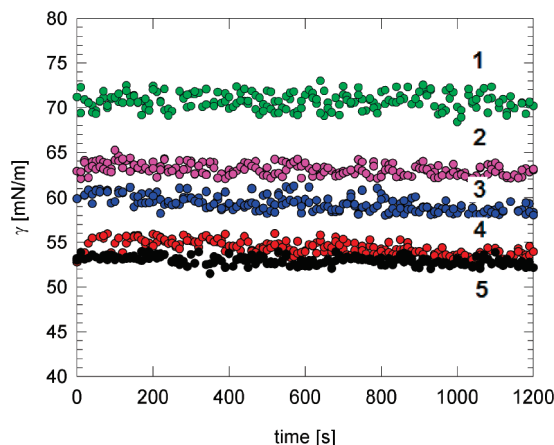


Figure 1. Surface tension (γ) of $C_{14}(\text{TAPABr})_2$ as a function of time (t) determined by the drop shape analysis method at various bulk surfactant concentrations, i.e., (1) 10^{-3} M, (2) 5×10^{-3} M, (3) 7×10^{-3} M, (4) 10^{-2} M, and (5) 2×10^{-2} M.

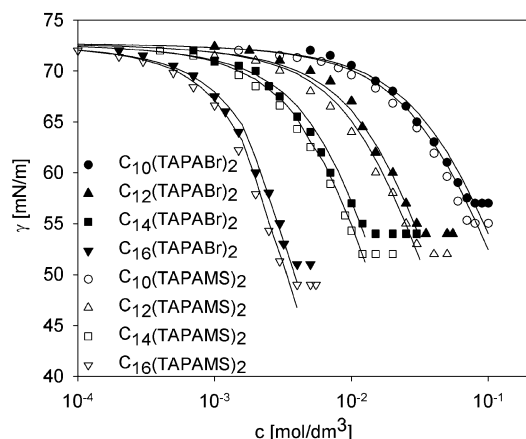


Figure 2. Surface tension (γ) of dicephalic dibromides $C_n(\text{TAPABr})_2$ and dimethylsulfates $C_n(\text{TAPAMS})_2$ ($n = 10, 12, 14, 16$) as a function of surfactant concentration. Lines represent fits of the theoretical model of ionic surfactant adsorption to experimental data. Best fit parameters are given in Table 1.

forward.⁴⁷ They represent a new group of bifunctional cationic surfactants, comprising one hydrophobic tail and two ammonium entities linked by a connector to a nitrogen bridge—a part of a functional labile amide group.

The surface activity of the studied compounds $C_n(\text{TAPABr})_2$ and $C_n(\text{TAPAMS})_2$ was characterized by surface tension measurements which were performed in a wide range of surfactant concentrations for all investigated compounds. Examples of kinetic adsorption (for $C_{14}(\text{TAPABr})_2$) are shown in Figure 1, proving that the adsorption equilibrium is established immediately. The absence of a long time drift of the surface tension can be considered as a proof of surfactant purity. The equilibrium surface tension isotherms for the aqueous solutions of $C_n(\text{TAPABr})_2$'s and $C_n(\text{TAPAMS})_2$'s are presented in Figure 2. The air–water surface tension γ vs $\log c$ reveals a classic behavior for surfactants, a steady decrease in γ , and a clean break with the absence of a minimum at the critical micelle concentration (cmc; values are in Table 1). The solid lines in Figure 2 represent fits of the theoretical model of ionic surfactant adsorption to experimental data, while the symbols denote experimental data. The best fit parameters (collected in Table 1) reveal that a good description of experimental surface tension isotherms was obtained. Increase of alkyl chain length in homologues series leads to the surface activity increase. The

$C_n(\text{TAPAMS})_2$'s are slightly more surface active than corresponding $C_n(\text{TAPABr})_2$'s. Differences in the surface activity between investigated bis-ammonium dibromides and dimethylsulfates can be interpreted in terms of the applied STDE model for the multiple charge surfactants (see the Introduction). The anion specific effects in the cationic surfactant adsorption can be explained by the different abilities of various anions to penetrate the surface Stern layer.^{25,56} Those anions that find their way through the surface layer more easily neutralize more effectively the charge of adsorbed surface active cations and diminish the surface potential of the electric double layer (EDL). As a result, the surface charge is being neutralized and, thus, more surfactant ions can be adsorbed at the interface. Thanks to the extended STDE model of the multiple charge surfactant adsorption, it is possible to correlate one of the model parameters “surfactant counterion surface activity”, α_c , with the ability of a given ion to penetrate the surface Stern layer. The lower the value of α_c , the easier it is for the counterion to penetrate the Stern layer. This means that, in the presence of surfactant cations, the methylsulfate ions ($\alpha_{\text{CH}_3\text{OSO}_3^-} = 2300 \text{ mol/dm}^3$) exhibit a higher affinity to the interface than the bromide ones ($\alpha_{\text{Br}^-} = 2800 \text{ mol/dm}^3$). Therefore, the methylsulfate ions can more effectively neutralize the electric field of the double layer at the interface, facilitating adsorption of surfactant ions and, thus, leading to lower surface tension. According to ref 25, the anions' ability to facilitate adsorption of cationic surfactants follows the following order: $\text{F}^- < \text{CH}_3\text{COO}^- < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{ClO}_4^-$, which coincides with the Hofmeister series of anion activity. The molecular dynamic simulations performed for monovalent electrolytes containing halide ions^{57–59} provided evidence that strongly polarized anions have the tendency to accumulate in the surface layer due to their interactions with the electric field at the interface. This tendency follows the Hofmeister series of anions and confirms the conclusions driven from the STDE model of ionic surfactant adsorption which concern the anion effect on the cationic surfactant surface activity. The value of the “surface activity” parameter for methylsulfate ions calculated from the STDE model indicates that they exhibit stronger interactions with the electric field at the interface than the NO_3^- ions ($\alpha_{\text{NO}_3^-} = 2500 \text{ mol/dm}^3$) and the Br^- ions ($\alpha_{\text{Br}^-} = 2800 \text{ mol/dm}^3$) and weaker than the I^- ions ($\alpha_{\text{I}^-} = 450 \text{ mol/dm}^3$).²⁵ It seems to be reasonable, since the polarizability of the methylsulfate counterions should be higher than that for HSO_4^- (whose surface activity was found to be similar to Cl^- ²⁶) due to their larger volume. The value of the methylsulfate anion polarizability has not been reported in the literature.

Dependence of the adsorption standard free energy ΔG_{ads}^0 on the number of carbon atoms, n_c , in the alkyl chain for both homologues series of dicephalic $C_n(\text{TAPABr})_2$ and $C_n(\text{TAPAMS})_2$ appears to be linear:

$$\Delta G_{\text{ads}}^0 = -2.96n_c + 10.69 \quad (12)$$

with the correlation coefficient $R^2 = 0.998$.

The values of ΔG_{ads}^0 (listed in Table 1) have been calculated as $\Delta G_{\text{ads}}^0 = RT \ln(\alpha_s)$, where α_s represents the “surface activity” of a given surfactant, defined in eq 2. This is in agreement with the classical Traube rule for the homologous series of surfactants.

To substantiate the hypothesis of the role of methylsulfate ions, we, additionally, performed measurements of the surface tension of solutions of the single head–single tail 3-[(trimethylammonio)propyl]dodecanamide bromide ($C_{12}\text{TAPABr}$) and 3-[(trimethy-

TABLE 1: Fitting Parameters^a of the Theoretical Model to the Surface Tension Isotherms of the Studied Dicephalic Cationic Surfactants and Their Linear Standards

compound	α_s (mol/dm ³)	H_s (kJ/mol)	$10^6 \Gamma_s$ (mol/cm ²)	A_{\min} (nm ²)	ΔG_{ads} (kJ/mol)	ϵ	K (m ³ /mol)	cmc ^b (mol/dm ³)
C ₁₀ (TAPABr) ₂	4.5×10^{-4}	0.5	3.4	0.49	-18.90	27	0.005	8.0×10^{-2}
C ₁₂ (TAPABr) ₂	3.6×10^{-5}	0.5	3.4	0.49	-25.10	26	0.005	3.5×10^{-2}
C ₁₄ (TAPABr) ₂	4.4×10^{-6}	0.5	3.4	0.49	-30.25	25	0.005	1.5×10^{-2}
C ₁₆ (TAPABr) ₂	2.9×10^{-7}	1.0	3.4	0.49	-36.92	22.5	0.005	4.0×10^{-3}
C ₁₀ (TAPAMS) ₂	4.5×10^{-4}	0.5	3.4	0.49	-18.90	27	0.007	7.5×10^{-2}
C ₁₂ (TAPAMS) ₂	3.6×10^{-5}	0.5	3.4	0.49	-25.10	26	0.007	3.0×10^{-2}
C ₁₄ (TAPAMS) ₂	4.4×10^{-6}	0.5	3.4	0.49	-30.25	25	0.007	1.0×10^{-2}
C ₁₆ (TAPAMS) ₂	2.9×10^{-7}	1.0	3.4	0.49	-36.92	22.5	0.007	3.5×10^{-3}
C ₁₂ TAPABr	1.6×10^{-5}	4.9	5.4	0.31	-27.08	26.5		1.2×10^{-2}
C ₁₂ TAPAMS	1.6×10^{-5}	4.9	5.4	0.31	-27.08	26.5		1.0×10^{-2}
DDTEABr ^c	7.2×10^{-6}	3.7	4.2	0.40				1.1×10^{-2}
d(DDA)EBR ^c	2.2×10^{-11}	3.6	4.1	0.41				8.5×10^{-4}
(bisAmC ₁₂)C ₂ ^d	2.2×10^{-11}	0.1	1.6	1.24		26	0.08	7.1×10^{-4}
(trisAmbisC ₁₂)C ₂ ^d	1.1×10^{-11}	0.5	1.5			26	0.30	

^a Other parameters: $\alpha_{\text{Br}^-} = 2800$ [mol/dm³], $\alpha_{\text{CH}_3\text{OSO}_3^-} = 2300$ [mol/dm³], $\delta = a_{\text{Br}^-} = 0.33$ [nm], $\delta = a_{\text{CH}_3\text{OSO}_3^-} = 0.35$ [nm]. ^b The cmc (critical micelle concentration) values are extracted from the surface isotherms (see Figures 1 and 2). ^c Data from ref 27. ^d Data from ref 11.

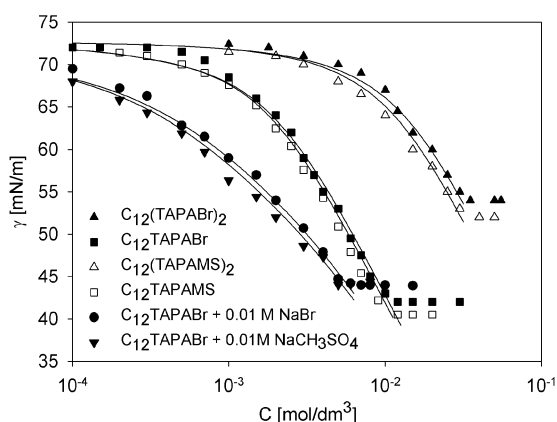


Figure 3. Surface tension (γ) of dicephalic compounds C₁₂(TAPABr)₂ and C₁₂(TAPAMS)₂ and their linear equivalents C₁₂TAPABr and C₁₂TAPAMS as a function of surfactant concentration. Surface tension (γ) of C₁₂TAPABr in the presence of added salts (10⁻² M NaBr and NaCH₃OSO₃) as a function of surfactant concentration. Solid lines denote theoretical curves.

lammonio)propyl]dodecanamide methylsulfate (C₁₂TAPAMS). In Figure 3, the surface tension isotherms for these surfactants are shown together with those obtained for the dicephalic bis-ammonium salts C₁₂(TAPABr)₂ and C₁₂(TAPAMS)₂ having the same hydrophobic chain length. Solid lines denote theoretical curves obtained from the multiple charge surfactant adsorption STDE model with the best fit parameters collected in Table 1. It can be seen that the single head—single tail surfactants are more surface active than the respective double charged (i.e., dicephalic) surfactants. This difference becomes evident also in relation to the standard free energy of adsorption, ΔG_{ads}^0 listed in Table 1. The more negative the ΔG_{ads}^0 values for linear derivatives C₁₂TAPABr and C₁₂TAPAMS, the higher their tendency to adsorb at the air/water interface in comparison to the dicephalic compounds. Moreover, the surfactant headgroup double charge makes it more hydrophilic and that remains in accord with much stronger repulsion between the electric surface charge of adsorbed dicephalic ammonium ions and those in the solution.

According to expectations, the surface area occupied by a surfactant at the interface, A_{\min} , calculated from the maximum value of the surface excess concentration Γ_{∞} , using the equation

$$A_{\min} = \frac{1}{N_A \Gamma_{\infty}} \quad (13)$$

(in which N_A is Avogadro's number and Γ_{∞} was calculated from the STDE model) is lower for the studied linear structures of C₁₂TAPABr or C₁₂TAPAMS compared to the dicephalic surfactants C₁₂(TAPABr)₂ and C₁₂(TAPAMS)₂. Moreover, no change of minimum surface area required per the adsorbed molecule along with increasing the surfactant alkyl chain length was observed for the latter structures. Considering the molecular structure of double-headed surfactants, one can conclude that the presence of two hydrophilic groups in the surfactant molecule increases the distance between alkyl chains in the adsorption layer and, therefore, decreases the lateral interaction between hydrophobic chains. This is also supported by a low value of the interaction parameter H_s for the dicephalic surfactants compared to their linear analogues. Only in the case of C₁₆(TAPABr)₂ and C₁₆(TAPAMS)₂ there are some weak interactions between very hydrophobic tails. The low value of the H_s parameter which points to the absence of significant hydrophobic interactions was also reported for bis- and tris-ammonium salts (i.e., bis[2-hydroxy-3-(dodecyltrimethylammonio)propyl]alkylamine dichlorides and bis[2-hydroxy-3-(dodecyltrimethylammonio)propyl]dialkylammonium trichlorides, (bisAmC₁₂)C₂, (bisAmC₁₂)C₆ and (trisAmbisC₁₂)C₂, (trisAmbisC₁₂)C₆, respectively)¹¹ with a different spacer length (cf. some representative data in Table 1). In the case of the studied and other described in the literature linear cationic derivatives, dodecyl trialkyl ammonium bromides (DDTABr, DDTEABr, DDTPABr, and DDTBABr), as well as gemini compounds, *N,N,N',N'*-tetramethyl-*N,N'*-di(dodecyl)alkylenedi-ammonium bromides (d(DDA)EBR, d(DDA)PBr, and d(DDA)B-Br)²⁷ (examples are listed in Table 1), the interaction parameter is relatively high in comparison with dicephalic surfactants and dimeric or trimeric-ammonium chlorides (structures are in ref 11). Moreover, for surfactants with differing sizes of the hydrophilic group, as in the case of dodecyl trialkyl ammonium bromides,²⁷ the value of the H_s parameter decreases with the size increase of the headgroup. The studied monomeric surfactants C₁₂TAPABr and C₁₂TAPAMS exhibit lower values of A_{\min} compared to the dicephalic C₁₂(TAPABr)₂ and C₁₂(TAPAMS)₂, as they occupy a smaller space at the air/water interface and, consequently, more surfactant molecules can be adsorbed there. The values of the A_{\min} parameter for DDTEABr, DDTPABr,

and DDTBABr containing bulky hydrophilic groups (see ref 27; examples are listed also in Table 1) are similar to those obtained for the studied dicephalics as well as for gemini derivatives (d(DDA)EBR, d(DDA)PBr, d(DDA)BBR),²⁷ whereas (bisAmC₁₂)C_n and (trisAmbisC₁₂)C_n ($n = 2, 6$)¹¹ show more than twice higher values of this parameter as a result of the geometrical structure of dimeric and trimeric surfactants.

Generally, adsorption of various surfactants at interfaces is determined by their structure, size, and number of the head groups, length and number of hydrophobic tails, etc., but in the case of cationic surfactant adsorption, the type of the counterion is of particular importance due to anion specific effects. The effect of methylsulfate vs bromide counterions upon the surface activity in the case of linear surfactants was similar to the one presented above for the dicephalic ones, i.e., C₁₂TAPAMS exhibiting higher surface activity than C₁₂TAPABr. The dependence of the surface tension on the C₁₂TAPABr surfactant concentration for fixed concentrations of NaBr (0.01 M) as well as NaCH₃OSO₃ (0.01 M) is shown in Figure 3. The obtained results prove that the addition of electrolytes produces the C₁₂TAPABr surface tension decrease and a stronger decrease appears in the presence of methylsulfate anions compared to the same concentration of bromide anions in the studied system. Evidently, the Br[−] ions in the solution of C₁₂TAPABr in 0.01 M CH₃NaOSO₃ are at least partially replaced at the interface by the methylsulfate anions and such a behavior proves that in the cationic surfactant solution the methylsulfate anions have a stronger affinity to the interface than the bromide ones. A similar phenomenon of anion replacement at the interface for CTABr and CTACl in the presence of KBr and KCl solutions was described in ref 25. In the presence of KBr, the decrease of surface tension of the above-mentioned surfactants is much higher than that in the solution containing the same amount of surfactant and KCl as the electrolyte. It is worth noting that the fitting procedure in the present contribution (solid lines in Figure 3 describe the theoretical results obtained from the STDE model) was performed by fixing the parameters for the bromide and methylsulphate anions at the values given in Table 1 for all isotherms presented in Figure 3. One can notice that all isotherms in a wide range of surfactant concentrations are described with a limited set of parameters. Recalling refs 40 and 48, it has to be emphasized that three of the mentioned parameters, namely, H_s , $\Gamma_{s\infty}$, and α_s , refer to the surfactant ions only. Thus, their physical meaning relates directly to the adsorption isotherm of nonionic surfactant which has the same chain length as the considered ionic one. Moreover, the value of limiting surfactant surface concentration $\Gamma_{s\infty}$ which is dependent on the size of the surfactant headgroup (not on the alkyl chain length), remains at the same level for all dicephalics along with the A_{\min} parameter, and differs from linear compounds C₁₂TAPABr and C₁₂TAPAMS as well as previously studied oligomeric structures.¹¹ The values of the α_s parameter (collected in Table 1) determine the appropriate surfactant activity. Similar to the surface activity of counterion parameter, α_c , the surface activity of surfactant is lower for higher surface activity of the molecule. In the calculations, we additionally assumed that effective ionic radii in the surface layer a_{Br^-} and $a_{CH_3OSO_3^-}$ determine the thickness of the Stern layer δ . There is no direct method to measure the dielectric constant in the Stern layer ϵ_s , but its value obtained in terms of the STDE model remains reasonable. A slight decrease of the dielectric constants with the increase of alkyl chain length is in agreement with results described in ref 60.

As demonstrated in our previous work,¹¹ for the oligomeric surfactants, there exists the possibility of formation of surfactant ion–counterion complexes, strongly influencing the interfacial properties of surfactant solutions. Therefore, the experimental surface tension isotherms of all cationic surfactants in the present study, comprising positively charged two quaternary ammonium headgroups and one hydrophobic chain (i.e., C_n(TAPABr)₂ and C_n(TAPAMS)₂; $n = 10, 12, 14, 16$), were interpreted in terms of the extended STD. One recalls that this model takes into account the multiple charges of surfactant molecules and the possibility of the formation of surfactant–counterion associates. As it has already been discussed, the formation of such associates can be described in terms of the mass action law (see eq 1):

$$K_{Br} = \frac{c_{surf^{2+}Br^-}}{c_{surf^{2+}}c_{Br^-}}, \quad c_s = c_{surf^{2+}} + c_{surf^{2+}Br^-}, \quad c_{Br^-} = 2c \quad (14)$$

where K_{Br} is the association constant (in the case of Br[−] counterions), C_{surf} the total surfactant concentration, $C_{surf^{2+}}$ the concentration of fully dissociated bis-ammonium surfactant, $C_{surf^{2+}Br^-}$ the concentration of surfactant–counterion associates, and C_{Br^-} the concentration of free bromide ions in the solution. Equation 13 allows one to determine the above-mentioned concentrations and make use of them in eqs 2–5 in order to account for the effect of associate formation on the surface tension of solutions. As is illustrated in Table 1, the best description of the experimental isotherms for the homologous series of C_n(TAPABr)₂ and C_n(TAPAMS)₂ surfactants was obtained for $K_{Br} = 5 \text{ dm}^3/\text{mol}$ and $K_{MS} = 7 \text{ dm}^3/\text{mol}$, respectively.

The hypothesis of the surfactant ion–counterion complex formation in the case of the studied dicephalic cationic surfactants has been theoretically supported both by molecular dynamics simulations for the C₁₂ representatives (e.g., C₁₂(TAPABr)₂ and C₁₂(TAPAMS)₂) and experimentally by measuring the concentration of free bromide ions in surfactant solutions using a Br[−] selective electrode. The results of the latter measurement obtained for C₁₂(TAPABr)₂, given as an example, are presented in Figure 4. For fully dissociated double charge surfactant molecules, the concentration of bromide ions present in the solution should be twice higher than the surfactant concentration, which is depicted by the dotted line in Figure 4. Experimental measurements show that the concentration of the Br[−] ions, at higher surfactant concentration (but still below its cmc), is lower than the predicted value for the fully dissociated surfactant molecules. The results of these experiments are well described by a theoretical dependence based on the solution of eq 14 with the association constant obtained for the best fit of the modified STDE adsorption model for multicharge surfactants to the experimental isotherm of C₁₂(TAPABr)₂. This indicates the formation of surfactant ion–bromide counterion associates, as was already observed and described for oligomeric cationic surfactants.¹¹ Existence of the surfactant ion–counterion complexes (values of their association constant K are placed in Table 1) in the case of the studied dicephalic surfactants causes partial neutralization of surfactant charge and results in the surface activity increase of C_n(TAPABr)₂ and C_n(TAPAMS)₂ ($n = 10, 12, 14, 16$) at the air/solution interface. For the lower surfactant concentrations, the amount of associates decreases in the solution, and for concentrations below 10^{−4} M, only fully dissociated surfactant ions are present in the aquatic system.

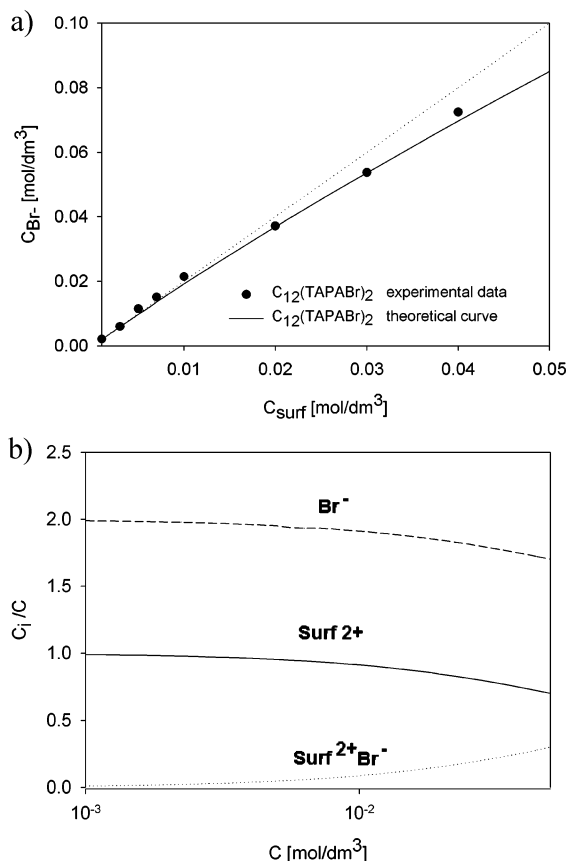


Figure 4. (a) Concentration of bromide ions in the solution of $C_{12}(TAPABr)_2$ as a function of surfactant concentration. Symbols denote experimental data, the solid line represents the theoretical dependence calculated according to eq 14, and the dotted line represents the hypothetical dependence in the absence of surfactant-counterion associates. (b) Relative amounts of divalent surfactant ions, bromide ions, and surfactant-bromide associates as a function of total surfactant concentration for $C_{12}(TAPABr)_2$ calculated according to eq 14.

Figure 5 presents optimized molecular structures of the representatives of studied surfactants, i.e., the dicephalic $C_{12}(TAPAX)_2$ and the linear $C_{12}TAPAX$ (X denotes bromide or methylsulfate counterion). Geometry optimization was performed with the Gaussian 03 quantum chemical modeling package.⁵² Characterization of the molecular structures (values of cross section of the hydrophilic part (nm^2), radius of gyration (nm), and other data for the same set of surfactants - placed in Table 2) was performed using their geometrical parameters and in relation to possible self-aggregation at the interfaces. The calculation of the hydrophobicity degree, defined as the logarithm of the compound octanol-water partition coefficient, $\log P$, was carried out with atomic parameters derived by Ghose et al.⁶¹ using the algorithm contained in the HYPERCHEM 7.5 chemical modeling package.⁴⁹ As it can be seen, the theoretically

calculated hydrophobicity (without taking into account electric charges) for the dicephalic surfactants is slightly lower than those obtained for their linear standards. Higher surface activity of the single head surfactants can also be explained taking into account cross sections of the hydrophilic parts, which are approximately twice higher for the dicephalics. Similar results were obtained from theoretical calculations, where surface area occupied by a surfactant at the interface, A_{min} (calculated from the maximum value of the surface excess concentration Γ_{∞}), is much higher for double-headed $C_{12}(TAPAX)_2$ than for its linear counterpart $C_{12}TAPAX$. Calculated values of radius of gyration depend on the chain length and are similar for both examined structures.

Molecular dynamics simulations of surfactant-counterion complexes were performed by the method described in detail in the Materials and Methods section for $C_{12}(TAPABr)_2$ and $C_{12}(TAPAMS)_2$ in the periodic box, whose size corresponded to the mean distance between surfactant molecules at concentrations of 10^{-3} , 5×10^{-3} , and 10^{-2} M. Figure 6 illustrates the dependence of the distance between Br^- and nitrogen atoms on the selected quaternary ammonium salts obtained during the simulations for surfactant concentration 10^{-3} M. The dotted line illustrates the limiting distance between these atoms corresponding to the surfactant and counterion in the associated state, which reflects the width of the energy minimum. If the distance between the counterion and at least one nitrogen is below that limit, the system is considered to be in the associated state. The probability of the surfactant-counterion association was calculated as the ratio of time when the system was in the associated state to the total simulation time. In Table 3, the probability of finding the surfactant and counterion in the associated state calculated from the molecular dynamic simulations for $C_{12}(TAPABr)_2$ and $C_{12}(TAPAMS)_2$ is compared with the relative concentration of surfactant-counterion associates with respect to total surfactant concentration. One can see that according to the mass action law the concentration of associates increases with total surfactant concentration. Our results also show that the methylsulfate anion has a stronger tendency to form associates with double-headed surfactants than bromide anion. The mechanism behind that tendency could be the same as the one for the larger decrease of the surface tension of cationic surfactants in the presence of methylsulfate salts, i.e., higher polarizability of methylsulfate anion and as a consequence stronger dispersive interactions. The distribution of the electronic negative charge over the oxygen atoms in the sulfate could also play a role in the strengthening of interactions between anion and quaternary ammonium grouping. Our results can be summarized by the conclusion that combining the STDE model of ionic surfactant adsorption and mass action law for the description of associate formation can provide a good description of the interfacial behavior of the studied cationic dicephalic (or double charge) surfactants.

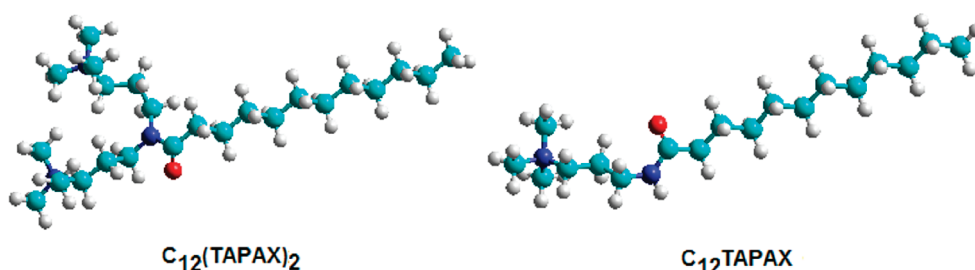


Figure 5. Molecular structures of the investigated surfactants; X denotes bromide or methylsulfate ions. The counterions are not shown.

TABLE 2: Characteristics of the Molecular Structures of the Studied Dicephalic Cationic Surfactants

parameter	C ₁₂ (TAPAX) ₂	C ₁₂ TAPAX
molecular mass	403.74	260.21
volume (Å ³)	1407.57	1133.79
log <i>P</i>	2.77	2.97
cross section of the hydrophilic part (nm ²)	40.47	20.26
radius of gyration (nm)	0.89	0.92

IV. Conclusions

The interfacial behavior of the studied dicephalic ammonium surfactants, *N,N*-bis[3,3'-(trimethylammonio)propyl]alkylamide dibromides and *N,N*-bis[3,3'-(trimethylammonio)-propyl]alkylamide dimethylsulfates, analyzed both experimentally and theoretically in comparison to their linear counterparts, 3-[(trimethylammonio)propyl]dodecanamide bromide and 3-[(trimethylammonio)propyl]dodecanamide methylsulfate, proves that their adsorption and the nature of the surfactant layer strongly depend on their structures. As a result of the much stronger repulsion between electric surface charges of dicephalic surfactant ions in the adsorption layer and in the solution, the single head–single tail surfactants are much more surface active than corresponding double charged compounds with the same alkyl chain length. Linear ammonium compounds exhibit lower values of *A*_{min} than corresponding dicephalic surfactants, because the presence of two hydrophilic groups in the surfactant molecule affects the distance between alkyl chains in the adsorption layer. They occupy more space at the interface, and consequently, only very weak lateral interactions between them can be observed. Moreover, the methylsulfate derivatives are slightly more surface active than the corresponding bromide compounds and they show better ability to lowering surface tension. Differences in the surface activity between investigated surfactants can be explained in terms of the different ability to penetrate the surface Stern layer by various anions, which coincides with the Hofmeister series effect. Anions, which can easily penetrate the surface layer, neutralize more effectively the charge of adsorbed surface active cations and lower the surface potential of the electric double layer (EDL). As a result of the surface charge neutralization, more surfactant ions can be adsorbed at the

TABLE 3: Probability of Finding the Surfactant and Counterion in the Associated State Calculated from the Molecular Dynamic Simulations for C₁₂(TAPABr)₂ and C₁₂(TAPAMS)₂

compound	concentration (mol/dm ³)	probability of associated state (MD simulation)	(<i>C</i> _{associated} / <i>C</i> _s) ^a
C ₁₂ (TAPABr) ₂	10 ^{−3}	0.01 ± 0.005	0.01
	5 × 10 ^{−3}	0.06 ± 0.01	0.047
	10 ^{−2}	0.08 ± 0.015	0.087
	2 × 10 ^{−2}	0.14 ± 0.02	0.156
C ₁₂ (TAPAMS) ₂	10 ^{−3}	0.01 ± 0.005	0.014
	5 × 10 ^{−3}	0.07 ± 0.01	0.063
	10 ^{−2}	0.10 ± 0.015	0.116
	2 × 10 ^{−2}	0.18 ± 0.02	0.20

^a Calculated from the STDE model applied to the surface tension isotherms.

interface. The theoretical calculation findings show that methylsulfate ions, due to their higher polarizability, exhibit stronger interactions with the electric field at the interface than Br[−] ions.

The modified “surface quasi-two-dimensional electrolyte” (STDE) model of ionic surfactant adsorption applied for the theoretical description takes into account counterion penetration to the adsorbed layer of double charge surfactant ions as well as the possibility of formation of surfactant ion–counterion associates in the solution. Bromide activity measurements indicated that the concentration of Br[−] ions, at higher surfactant concentration but still below their cmc's, was lower than that predicted for fully dissociated surfactant molecules. This phenomenon was also confirmed by molecular dynamic simulations, which also demonstrated that methylsulfate ions had a higher tendency to form associates with the investigated dicephalic surfactants than the bromide ones. These results supported all conclusions drawn from the description of surface tension isotherms of bis-ammonium dicephalic dibromides and dimethylsulfates in terms of the STDE model of ionic surfactant adsorption.

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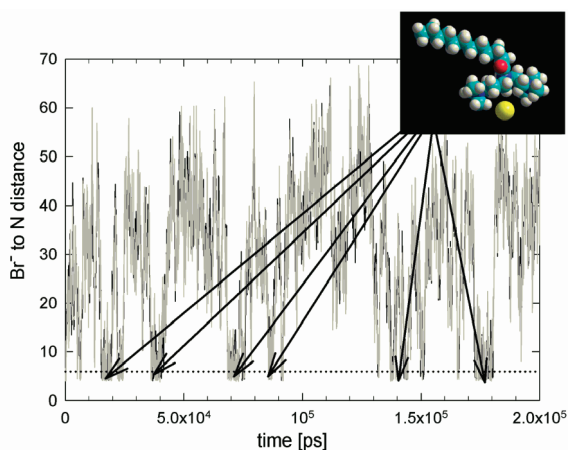


Figure 6. Dependence of the distance between Br[−] and nitrogen atoms of quaternary amines (black and gray lines, respectively) obtained during the molecular dynamics simulations for 10^{−3} M C₁₂(TAPABr)₂ surfactant concentration. The dotted line illustrates the limiting distance between these atoms corresponding to the surfactant and counterion in the associated state. Arrows indicate periods when the system is in the associated state.

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