

Received May 08, 2017; reviewed; accepted August 04, 2017

## Nonequivalent adsorption of pH-responsive dicephalic sugar surfactants at the air/solution interface

Łukasz Lamch<sup>1</sup>, Anna Jarzycka<sup>1</sup>, Lilianna Szyk-Warszyńska<sup>2</sup>, Piotr Warszyński<sup>2</sup>, Kazimiera A. Wilk<sup>1</sup>

<sup>1</sup> Department of Organic and Pharmaceutical Technology, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

<sup>2</sup> J. Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

Corresponding author: ncwarszy@cyf-kr.edu.pl (Piotr Warszyński)

**Abstract:** The present work contributes to the analysis of the effect of electrolyte and pH on the adsorption of dicephalic *N*-dodecyl-*N,N*-bis[(3-*D*-aldonylamido) propyl]amines (aldonyl = gluconyl and lactobionyl) at the air/water interface. The headgroup of these surfactants consists of two amide groups connected by a central tertiary amine, which may be protonated in an aqueous environment. We performed measurements of surface tension isotherms of aqueous solutions of the studied dicephalics in the presence of NaCl and NaOH and applied the STDE model for evaluation of the experimental results. They showed that the adsorption of the surfactants at the air/water interface was pH- and electrolyte- dependent, since addition of NaCl and NaOH had different effects on the surface activity and critical micelle concentration values (CMC). The theoretical model reflected well the surface tension isotherms obtained for a broad range of surfactants concentration, confirming the theoretical predictions concerning the protonation of tertiary amines, which was additionally supported by the measurements of solution pH.

**Keywords:** bis-aldonamide surfactants, adsorption, STDE model, pH, electrolyte influence

### 1. Introduction

The search for environmentally-friendly surfactants, derived from natural resources, and a basic understanding of their self-aggregation phenomena at the interfaces and in a solution are of a particular interest due to their potential applications as new cosmetic formulations, drug delivery systems, gene therapy as well as biomedically or bioanalytically-oriented specialty products (Luk and Abbot, 2002; Foley et al., 2012). The introduction of carbohydrate species into the polar building block of the surfactant structure has given a great opportunity to researchers to gain new interesting physico-chemical properties including surface and colloid properties, micellization, phase behaviour or microemulsification and biological functionalities (Söderman and Johansson, 2000; Holmberg, 2001; Carneto Ruiz, 2008; Claesson and Kjellin, 2008; Wilk et al., 2011).

An important feature of sugar based surfactants is the temperature insensitivity of their surface and aggregation properties resulting from the strength of the hydrogen bonds between the hydroxyl groups of the carbohydrate-based amphiphiles and water (Stubenrauch, 2001; Zielińska et al., 2008). It has to be emphasized that even slight modifications of the saccharide-derived unit – present in their molecular structure – make possible to create a wide physicochemical behavior spectrum of new surfactants different from the conventional ones (van Doren et al., 2000; Burczyk et al., 2001; Komorek and Wilk, 2004; Carneto Ruiz, 2008). Most of so-called sugar surfactants were found to exhibit profound surface adsorption properties and they may form micelles at exceptionally low concentrations (Johansson and Engberts, 2004; Wilk et al., 2011). Such structures can also generate a

broad spectrum of aggregate morphologies resembling biological systems, e.g., micelles, vesicles, bilayers, fibers and gels, thermotropic liquid crystalline phases in their pure state upon heating and lyotropic liquid crystalline phases upon addition of a solvent (Stubenrauch, 2001; Estroff and Hamilton, 2004; Johnsson and Engberts, 2004; Laska et al., 2006). In particular, they may exhibit pH dependent transition between different aggregate forms (Johnsson et al. 2003).

In our present contribution the effects of electrolytes and pH on the adsorption of *N*-dodecyl-*N,N*-bis[(3-*D*-aldonylamido)propyl]amines at the air/water interface have been investigated. The studied aldonamide-type surfactants (Wilk et al., 2000; 2009), obtained in a straightforward three-step procedure from readily available, inexpensive reagents, represent a family of biodegradable molecules with dicephalic architecture, which is composed of one hydrophobic tail and two hydrophilic aldonamide-type groupings (gluconyl C12-DGA or lactobionyl C12-DLA) linked by the propylene chain at the nitrogen atom (for their structures see Fig. 1). Thus, we selected two surfactants that consist of two amide groups and a central tertiary amine, which may be protonated, oxidized to the corresponding amine oxide, or quaternized to give a permanent cationic charge to the surfactant. Each of the mentioned reactions may lead to both an increase in their solubility and the physical-chemical properties modulation. The adsorption properties of these surfactants at the water/air interface was studied previously (Oskarsson et al., 2007) but without any attempt to describe them in terms of a theoretical model. We performed measurements of surface tension isotherms of aqueous solutions of C12-DGA and C12-DLA in the presence of NaCl or NaOH. For the evaluation of the experimental findings we applied the theoretical model of a "surface quasi-two-dimensional electrolyte" (STDE), which has been also used for the description of ionic and nonionic surfactant mixtures (Jarek et al., 2006). The STDE theoretical background is described in the discussion part of our contribution.

## 2. Experimental

### 2.1 Materials

*n*-Dodecylamine, *D*(+)-gluconic  $\delta$ -lactone and lactobionic acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). 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.

The sugar-derived surfactants - *N*-dodecyl-*N,N*-bis[(3-*D*-gluconylamido)propyl]-amine (C12-DGA) and *N*-dodecyl-*N,N*-bis[(3-lactobionylamido)propyl]-amine (C12-DLA) were obtained in a multistep processes. The first two steps (synthesis of *N*-dodecyl-*N,N*-bis(2-cyanoethyl)amine (C12-CN) and *N*-dodecyl-*N,N*-bis(3-aminopropyl)amine (C12-NH<sub>2</sub>)) were the same for both surfactants. C12-CN was synthesized via Michael addition of *n*-dodecylamine to acrylonitrile, according to a modified procedure of the previously published synthesis route (Wilk et al., 2000). Reduction of C12-CN to C12-NH<sub>2</sub> was carried out in modified Bouveault-Blanc conditions. Thus, C12-CN (20 g, 69 mmol) was dissolved in anhydrous isopropanol (350 cm<sup>3</sup>) and metallic sodium (40 g, 1.7 mol) was slowly added over a 45-min interval with vigorous stirring. After complete addition of sodium the mixture was refluxed for 3 h followed by the alcohol removal under reduced pressure. The residue was dissolved in distilled water (150 cm<sup>3</sup>) and extracted with diethyl ether (3 x 75 cm<sup>3</sup>). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and diethyl ether was evaporated off. The crude product was purified by vacuum distillation (217 °C, 2 mbar), yielding 15.4 g of C12-NH<sub>2</sub> (74%).

*Synthesis of C12-DGA*: C12-NH<sub>2</sub> (15 g, 50 mmol) and *D*(+)-gluconic  $\delta$ -lactone (18.4 g, 103 mmol) were dissolved in dry methanol (150 cm<sup>3</sup>) and stirred for 48 h at room temperature. After completion of reaction the obtained mixture was cooled to 5°C, followed by the precipitated solid filtration and washing with cold ethanol. The crude product was dried *in vacuo* over KOH and recrystallized several times from ethanol to give C12-DGA. Yield: 84% (mp 167-170.3 °C). Analysis calculated for C<sub>30</sub>H<sub>61</sub>O<sub>12</sub>N<sub>3</sub>: C, 54.94; H, 9.37; N, 6.41; found: C, 55.0; H, 9.37; N, 6.40. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ <sub>H</sub> 7.66 (2H, CONH); 4.30-5.33 (10H, OH groups from sugar part); 3.89-3.98 and 3.36-3.55 (10H, (OHCH) and -CH<sub>2</sub>OH); 3.07-3.10 (4H, CONH-CH<sub>2</sub>); 2.25-2.36 (6H, -CH<sub>2</sub>N(CH<sub>2</sub>)CH<sub>2</sub>-); 1.49-1.54 (4H, CONH-CH<sub>2</sub>CH<sub>2</sub>); 1.35 (2H, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>); 1.22 (18H, CH<sub>2</sub>-(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>); 0.84 (3H, (CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>). C12-DLA was obtained and purified as it was described for C12-DGA, in reaction of C12-NH<sub>2</sub> (15 g, 50 mmol) with lactobionic acid (37.0 g, 103 mmol). Yield: 75%. Analysis calculated for C<sub>42</sub>H<sub>81</sub>O<sub>22</sub>N<sub>3</sub>: C,

51.47; H, 8.33; N, 4.29; found: C, 51.55; H, 8.40; N, 4.32.  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ):  $\delta_H$  7.62 (2H, CONH); 4.64–5.14 (16H, OH groups from sugar part); 3.38–4.06 (12H, from sugar part); 3.08 (4H, CONH- $\text{CH}_2$ ); 2.31–2.33 (6H,  $-\text{CH}_2\text{N}(\text{CH}_2)\text{CH}_2$ ); 1.51 (4H, CONH- $\text{CH}_2\text{CH}_2$ ); 1.35 (2H,  $\text{NCH}_2\text{CH}_2(\text{CH}_2)_9$ ); 1.23 (18H,  $\text{CH}_2-(\text{CH}_2)_9-\text{CH}_3$ ), 0.82 (3H,  $(\text{CH}_2)_9-\text{CH}_3$ ). The detailed identification and structural analysis of C12-DGA and C12-DLA was described by Wilk et al. (2000). Molecular structures of surfactants are shown in Figure 1.

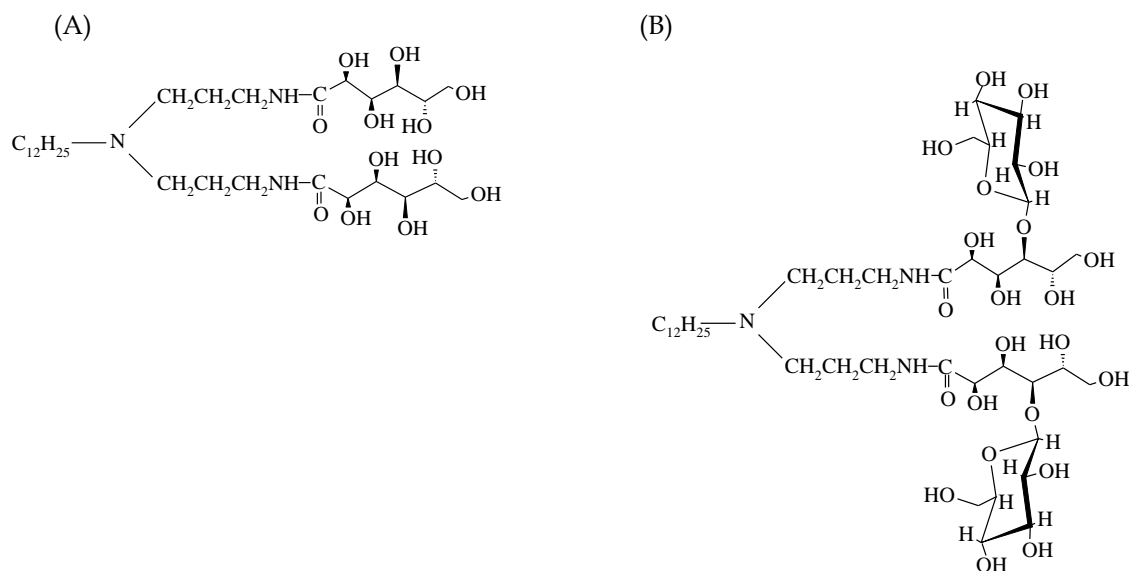


Fig. 1. Structures of the investigated dicephalic surfactants: A. N-dodecyl-N,N-bis[(3-D-gluconylamido)propyl]-amine (C12-DGA) and B. N-dodecyl-N,N-bis[(3-lactobionylamido)propyl]-amine (C12-DLA)

## 2.2 Surface tension measurements

The air-water surface tension ( $\gamma$ ) was measured using the Krüss K12 automatic tensiometer (Hamburg, Germany) equipped with the du Nuoy Pt-Ir ring at  $25 \pm 0.1^\circ\text{C}$ . Sets of surface tension measurements were taken at preselected intervals until no significant change occurred in the tension. The pull method was employed, and the ring did not become detached from the surface. The  $\gamma$  vs. concentration data were averages of two independent runs. Equilibrium surface tension data were reproducible within  $0.5 \text{ mN m}^{-1}$ .

## 3. Results and discussion

### 3.1 Theoretical background

The investigated N-dodecyl-N,N-bis[(3-D-aldonylamido)propyl]amines contain two amide groups and a central tertiary amine, which may be protonated in acidic and neutral conditions to form a monocation that results in increase of surfactant solubility and CMC, whereas, the ability to decrease surface tension at water/air interface should be diminished. The solution contains both neutral C12-DGA or C12-DLA molecules and their positively charged ionic protonated forms (cf. Figure 2).

For the description of the adsorption properties of the investigated surfactants we used the “surface quasi-two-dimensional electrolyte” (STDE) model which was developed by Warszyński et al. (Warszynski et al., 2002; Para et al., 2006) to describe quantitatively the surface tension isotherms of ionic surfactants in the presence of various electrolytes. The model was also extended to describe the adsorption of surfactant mixtures, including non-ionic and ionic (Jarek et al., 2006). It has been also successfully applied to characterize the adsorption of multifunctional cationic surfactants (Węgrzyńska et al., 2008; Skrzela et al., 2010) as well as cleavable esterquat surfactants (Para et al., 2016). The main features of the STDE model proposed previously are presented in Figure 3. Adsorption of the ionic surfactants at the air/electrolyte or oil/electrolyte interfaces leads to

formation of the electric double layer. Surfactant head-groups and counterions of any type can be present in the Stern layer. They preserve their freedom of motion and therefore, the Stern layer can be considered as a quasi two-dimensional electrolyte, which does not fulfil the electroneutrality condition. On the other hand, adsorption of non-ionic surfactants is not affected by the presence of charge at the interface.

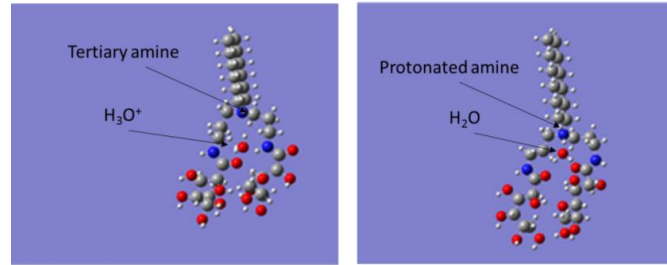


Fig. 2. Protonation of C12-DGA resulting in formation of mixture of non-ionic and ionic surfactants

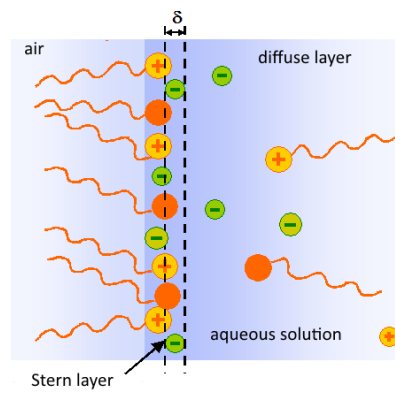


Fig. 3. Scheme of the STDE model of adsorption

Equations of adsorption for all components of the system were derived from the condition of equal chemical potential at the surface and in the bulk. They take the following form:

$$\frac{a_{is}}{\alpha_s} \exp\left(-\frac{e\psi_s}{kT}\right) (1 - \theta_{is} - \theta_c - \theta_{ns})^{g_{is}} = \theta_s \exp(-2H_s(\theta_{is} + \theta_{ns})) \exp\left(\frac{\varphi_s}{kT}\right), \quad (1)$$

$$a_{is} = \alpha_i f_{is} c_s$$

for a protonated (cationic) surfactants,

$$\frac{a_c}{\alpha_c} \exp\left(\frac{e\psi_s}{kT}\right) (1 - \theta_{is} - \theta_c - \theta_{ns})^{g_{cs}} = \exp\left(\frac{\varphi_c}{kT}\right), \quad (2)$$

$$a_c = f_c c_c$$

for counterions,

$$\frac{c_{ns}}{\alpha_s} (1 - \theta_{is} - \theta_c - \theta_{ns})^{g_{ns}} = \theta_{ns} \exp(-2H_s(\theta_{is} + \theta_{ns})), \quad (3)$$

$$c_{nc} = (1 - \alpha_i) c_s$$

for nonionic surfactant molecules.

The symbols in the equations above denote:  $a_{is}$ ,  $a_c$  the activities of surfactant ions and counterions (hydroxyl or hydrocarbonate) and  $f_{is}$ ,  $f_c$  are respective activity coefficients, which can be calculated from extended Debye - Hückel theory of strong electrolyte solutions,  $c_s$  is bulk

concentration of surfactant,  $\alpha_i$  is the degree of its ionization,  $\theta_s = \Gamma_{is} / \Gamma_{s\infty}$  is the relative protonated surfactant surface concentration, where  $\Gamma_{is}$  is its surface (excess) concentration and  $\Gamma_{s\infty}$  is the limiting surfactant surface concentration for both non-ionic and ionic form of the closely packed monolayer,  $\theta_c = \Gamma_c / \Gamma_{c\infty}$ ,  $\theta_{ns} = \Gamma_{ns} / \Gamma_{ns\infty}$ ,  $\Gamma_c$ ,  $\Gamma_{ns}$  and  $\Gamma_{c\infty}$  are the same quantities for counterion and neutral surfactant molecule,  $g_{is}$ ,  $g_{cs}$  and  $g_{ns}$  are the ratio of the size of surfactant ion, counterion and neutral surfactant relatively to the size of the adsorption site ( $g_{is} = g_{ns} = 1$ ) for the sake of simplicity),  $H_s$  is the surface interaction parameter accounting mainly for the attractive lateral interactions among the adsorbed surfactant hydrophobic tails,  $\alpha_s$  is the "surface activity" of surfactant, being a measure of the standard free energy of adsorption after separating the contribution of the electric component, i.e., the same for the protonated and non-protonated form,  $\alpha_c$  is the "surface activity" of counterion which is a measure of its affinity to the surface layer,  $\phi_s$ ,  $\phi_c$  are the corrections for the activity of the two dimensional electrolyte in the surface layer accounting for the lateral interaction between ions discussed in details elsewhere (Warszynski et al. 2002, Para et al., 2006).

The electric potential of the Stern layer can be found from:

$$\psi_s = \psi_d + \frac{\sigma \delta}{\epsilon_0 \epsilon_s} \quad (4)$$

where the diffuse layer potential at the boundary between the Stern layer and the diffuse part of electric double layer can be determined from the formula:

$$\psi_d = \frac{2kT}{e} \sinh^{-1} \left( \frac{\sigma e}{2 \epsilon_0 \epsilon k T \kappa} \right), \quad (5)$$

where:  $e$  is the elementary charge,  $k$  is the Boltzmann constant,  $\epsilon_0$  is the vacuum dielectric permittivity,  $\epsilon$  is the dielectric constant of the solution,  $\kappa$  is the Debye - Hückel reciprocal length,  $\sigma = F(\Gamma_s - z_c \Gamma_c)$  is the surface charge density, where  $z_c$  are valences of counterions,  $F$  is the Faraday constant,  $\delta$  is the thickness of the Stern layer and  $\epsilon_s$  is the dielectric constant in the Stern layer.

The procedure of solving Eqs. 6-10 and the detailed interpretation of parameters were described before (Warszynski et al., 2002; Para et al., 2006). By the numerical solution of the system of equations the surface concentration of the surfactant ions, counterions, and nonionic surfactant molecules can be determined directly. Total surface excess concentration has to include adsorption of counterions and surfactant ions (here assumed negative) in the diffuse part of the electric double layer and can be calculated as:

$$\Gamma_+ = \Gamma_{is} + \int_0^\infty (c_+(x) - c_{+b}) dx, \quad (6)$$

$$\Gamma_- = \Gamma_c + \int_0^\infty (c_-(x) - c_{-b}) dx, \quad (7)$$

where the integration involves all ions present in the solution.

The surface tension isotherm can be predicted by integration of the Gibbs equation for mixture of ionic-nonionic surfactant:

$$d\gamma = -RT(\Gamma d \ln a. + \Gamma_+ d \ln a_+ + \Gamma_{ns} dc_{ns}). \quad (8)$$

From the fit of the calculated isotherm to the experimental data the parameters of the model for investigated system can be obtained.

In order to determine the dependence of the degree of protonation of C12-DGA or C12-DLA on their concentration we measured the pH of their solution and described the experimental curves, illustrated in Fig. 4., in terms of the mass action law taking into account the effect of dissolved CO<sub>2</sub>.

The resulting  $pK_a$  were  $8.1 \pm 0.2$  and  $8.0 \pm 0.2$  for C12-DGA and C12-DLA, respectively, in a good agreement with the values obtained before (8.4 and 8.0) (Oskarsson et al., 2007).

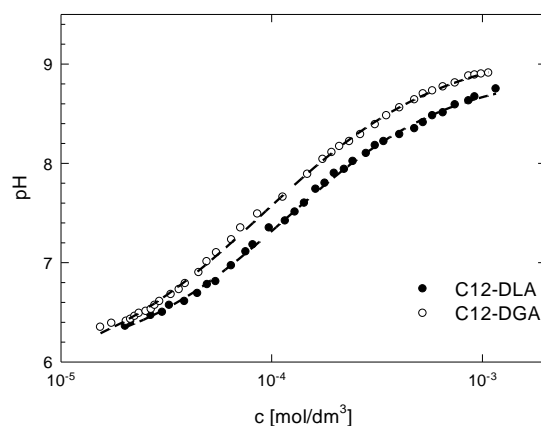


Fig. 4. Dependence of pH of C12-DGA and C12-DLA on their concentration in solution. Lines denote fitted curves

### 3.2 Surface tension isotherms

Figures 5 and 6 illustrate surface tension isotherms of C12-DGA and C12-DLA surfactants respectively, determined for water and 1 mM solutions of NaCl and NaOH. Lines represent fits of the STDE model of adsorption to experimental data. It is necessary to stress that to describe the data obtained for those three different experimental conditions (as shown in the Figures 5 and 6) fit of only two parameters characterizing surfactant molecule  $\alpha_s$  and  $\Gamma_{s\infty}$  was necessary, while other parameters were either derived following experimental conditions (including the protonation degree assuming the values of  $pK_a$  determined as above) or calculated independently before for other surfactant systems (Para et al., 2006) as ones concerning counterions or the Stern layer. The values of the best fit parameters are given in Table 1. The results presented in Figs. 5 and 6 indicate that in water C12-DLA is slightly more hydrophilic (less surface active) than C12-DGA as it contains two additional galactose rings in the structure of the dicephalic headgroup. The CMC values are  $8 \times 10^{-4}$  mol/dm<sup>3</sup> and  $3 \times 10^{-4}$  mol/dm<sup>3</sup> respectively, in the good agreement with the results obtained previously (Wilk et al., 2000). Surprisingly that difference in the headgroup molecular structure is only weakly reflected as the fitted area per molecule at CMC,  $A_{CMC} = 1/(N_A \Gamma_{CMC})$  is similar 0.6 nm<sup>2</sup> for C12-DLA and 0.51 nm<sup>2</sup> for C12-DGA.

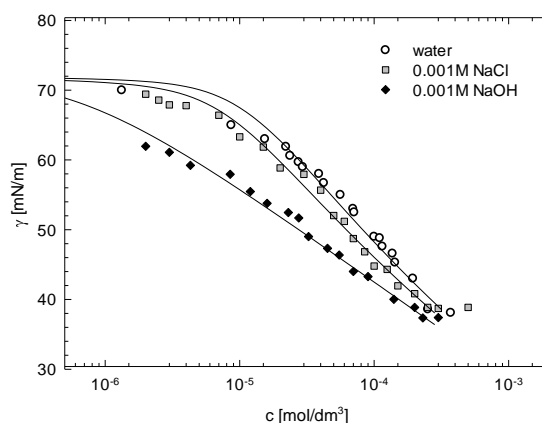


Fig. 5. Surface tension isotherms of C12-DGA in water and 1 mM solutions of NaCl and NaOH

Addition of 1 mM NaCl leads to a minor decrease of surface tension. Since addition of salt induces the shielding effect on the surface charge of adsorbed ionic surfactant layer (Para et al., 2007) we can conclude that the decrease of surface tension is mostly determined by adsorption of neutral form of

surfactants. On the other hand, addition of 1 mM of NaOH has the major effect on the surface tension decrease at low surfactant concentration. In basic conditions the protonation of the tertiary amine is suppressed and the non-ionic form dominates the adsorption in the whole range of surfactant concentrations. The calculated dependence of the protonation on the concentration of the investigated surfactant in water and 1mM NaOH is illustrated in Fig. 7.

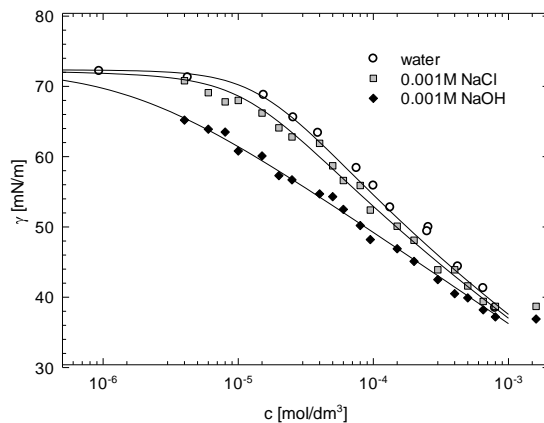


Fig. 6. Surface tension isotherms of C12-DLA in water and 1 mM solutions of NaCl and NaOH

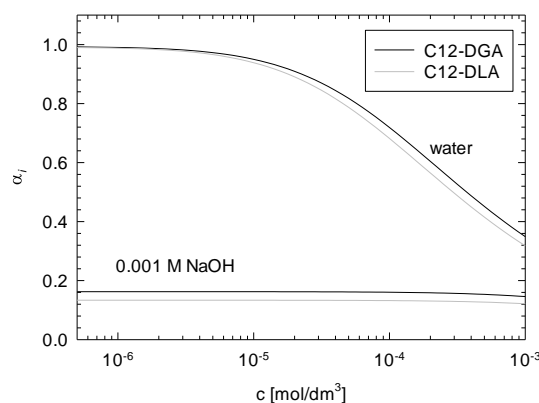


Fig. 7. Dependence of the degree of protonation of the tertiary amine for C12-DGA and C12-DLA on their concentration in solution used for the STDE model

Table 1. The values of the best fit parameters of the STDE model of adsorption to experimental data

Parameter	Best-fit values	
	C12-DGA	C12-DLA
$\alpha_S$ [mol/dm <sup>3</sup> ]	$5.5 \pm 1.0 \times 10^{-7}$	$1.5 \pm 0.3 \times 10^{-6}$
$\Gamma_{S\infty}$ [mol/cm <sup>2</sup> ]	$2.4 \pm 0.2 \times 10^{-10}$	$2.3 \pm 0.2 \times 10^{-10}$
$\chi^2$	5.5	6.8
Other parameters		
$H_S$ [kJ/mol]	0	0
$\epsilon_s$	26	26
$g_{OH^-}$	0.25	0.25
$g_{Cl^-}$	0.20	0.23
$a_{OH^-}$ [mol/dm <sup>3</sup> ]	55	55
$a_{Cl^-}$ [mol/dm <sup>3</sup> ]	15000	15000
$a_{Cl^-}$	0.35	0.35
$\delta = a_S$ [nm]	0.45	0.45

#### 4. Conclusions

According to the acquired data for the surface tension isotherms, the adsorption process of dicephalic *N*-dodecyl-*N,N*-bis[(3-*D*-aldonylamido) propyl]amines (aldonyl as gluconyl (C12-DGA) and lactobionyl (C12-DLA)) at the air/water interface was found to be pH- and electrolyte- dependent, however, addition of NaCl and NaOH had different effect on the surface tension magnitude and critical micelle concentration values (CMC) of the dicephalic aldonamide-type surfactants solution. Presence of 0.001M NaCl had a relatively minor influence on the surface tension isotherm in comparison to pure surfactant solution. On the other hand, presence of 0.001 M NaOH caused substantial reduction of surface tension and much smaller reduction of the CMC value. The theoretical model based on the STDE model of adsorption of ionic-non-ionic surfactant mixtures reflected well the surface tension isotherms obtained for a broad range of surfactants concentration, confirming the theoretical predictions concerning protonation of tertiary amine, which was additionally corroborated by the measurements of surfactant solution pH.

#### Acknowledgements

This work has been supported by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Science and Technology and by the Marian Smoluchowski Krakow Research Consortium – a Leading National Research Centre KNOW.

#### References

- BURCZYK B., WILK K.A., SOKOŁOWSKI A., SYPER L., 2001. *Synthesis and surface properties of N-alkyl-N-methylgluconamides and N-alkyl-N-methylactobionamides*. J. Colloid Interface Sci., 240, 552-558.
- CARNERO RUIZ, C., 2008. *SugarBased surfactants. Fundamentals and applications*. Taylor & Francis, New York, U.S.A.
- CLAESSON M., KJELLIN U.R.M., 2006. *Sugar surfactants*. in: SOMASUNDARAN P., HUBBARD A. (Eds.), *Encyclopedia of Surface and Colloid Science*, Taylor & Francis, New York, U.S.A.
- DOREN VAN H. A., SMITS E., PESTMAN J.M., ENGBERTS J.B.F.N., KELLOGG R.M., 2000. *Mesogenic sugars. From aldoses to liquid crystals and surfactants*. Chem. Soc. Rev., 29, 183-199.
- ESTROFF L.A., HAMILTON A.D., 2004. *Water gelation by small organic molecules*. Chem. Rev., 104, 1201-1217.
- FOLEY P., KERMANSHAH A., BEACH E. S. ZIMMERMAN J. B., 2012. *Derivation and synthesis of renewable surfactants*. Chem. Soc. Rev., 41, 1499-1518.
- Holmberg K., 2001. *Natural surfactants*, Curr. Opin. Colloid Interface Sci., 6, 148-157.
- JAREK E., WYDRO P., WARSZYŃSKI P., PALUCH M., 2006. *Surface properties of mixtures of surface-active sugar derivatives with ionic surfactants: Theoretical and experimental investigations*. J. Colloid Interface Sci., 293, 194-202.
- JOHNSSON M., ENGBERTS, J.B.F.N., 2004. *Novel sugar-based gemini surfactants: aggregation properties in aqueous solution*. J. Phys. Org. Chem., 17, 934-944.
- JOHNSSON M., WAGENAAR A., STUART M. C. A., ENGBERTS, J. B. F. N., 2003. *Sugar-based gemini surfactants with pH-dependent aggregation behavior: Vesicle-to-micelle transition, critical micelle concentration, and vesicle surface charge reversal*. Langmuir, 19, 4609-4618.
- KOMOREK U., WILK K.A., 2004. *Surface and micellar properties of new nonionic gemini aldonamide-type surfactants*. J. Colloid Interface Sci., 271, 206-211.
- LASKA U., WILK K.A., MALISZEWSKA I., SYPER L., 2006. *Novel glucose- derived gemini surfactants with 1,1'ethylenebisurea spacer: preparation, thermotropic behavior and biological properties*. J. Surfactants Deterg., 9, 115-124.
- LUK Y.-Y., ABBOTT N.L., 2002. *Applications of functional surfactants*. Curr. Opin. Colloid Interface Sci., 7, 267-275.
- OSKARSSON H, FRANKENBERG M, ANNERLING A, HOLMBERG K., 2007. *Adsorption of Novel Alkylaminoamide sugar surfactants at tailor-made surfaces*. J. Surfactants Deterg., 10, 41-52
- PARA G., JAREK E., WARSZYŃSKI P., 2006. *The Hofmeister series effect in adsorption of cationic surfactants – theoretical description and experimental results*. Adv. Colloid Interface Sci., 122, 39-55.



- PARA G., ŁUCZYŃSKI J., PALUS J., JAREK E., WILK K.A., WARSZYŃSKI P., 2016. *Hydrolysis driven surface activity of esterquat surfactants*. J. Colloid Interface Sci., 465, 174-182.
- SKRZELA R., PARA G., WARSZYŃSKI P., WILK K.A., 2010. *Experimental and theoretical approach to nonequivalent adsorption of novel dicephalic ammonium surfactants at the air/solution interface*. J. Phys. Chem. B, 114, 10471-10480.
- SÖDERMAN O., JOHANSSON I., 2000. *Polyhydroxyl-based surfactants and their physico-chemical properties and applications*. Curr. Opin. Colloid Interface Sci., 4, 391-401
- STUBENRAUCH C., 2001. *Sugar surfactants - aggregation, interfacial, and adsorption phenomena*. Curr. Opin. Colloid Interface Sci., 6, 160-170.
- WARSZYŃSKI P., LUNKENHEIMER K., CZICHOCKI G., 2002. *Effect of counterions on the adsorption of ionic surfactants at fluid fluid Interfaces*. Langmuir, 18, 2506-2514.
- WĘGRZYŃSKA J., PARA G., CHLEBICKI J., WARSZYŃSKI P., WILK K.A., 2008. *Adsorption of Multiple Ammonium Salts at the Air/Solution Interface*. Langmuir, 24, 3171-3180.
- WILK K. A., LASKA U., ZIELIŃSKA K., OLSZOWSKI A., 2011. *Fluorescence probe studies upon microenvironment characteristics and aggregation properties of gemini sugar surfactants in an aquatic environment*. J. Photochem. Photobiol., A, 219, 204-210.
- WILK K.A., SYPER L., BURCZYK B., SOKOLOWSKI A., DOMAGALSKA B., 2000. *Synthesis and surface properties of new dicephalic saccharide - derived surfactants*. J. Surfactants Deterg., 3, 185-192.
- WILK K.A., ZIELIŃSKA K., JEZIEŃSKI A., 2009. *Structural aspects in saccharide-derived micelles studied by a spin probe technique*. Colloids Surf., A, 343, 64-69.
- ZIELIŃSKA K., WILK K.A., JEZIEŃSKI A., JESIONOWSKI T., 2008. *Microstructure and structural transition in microemulsions stabilized by aldonamide - type surfactants*. J. Colloid Interface Sci., 321, 408-417.