

## Aggregation behavior of dicephalic di-N-oxide surfactants in aqueous solution: Experimental and computational approaches



Agnieszka Lewińska<sup>a</sup>, Maciej Witwicki<sup>a</sup>, Urszula Bazylińska<sup>b</sup>, Adam Jezierski<sup>a</sup>, Kazimiera A. Wilk<sup>b,\*</sup>

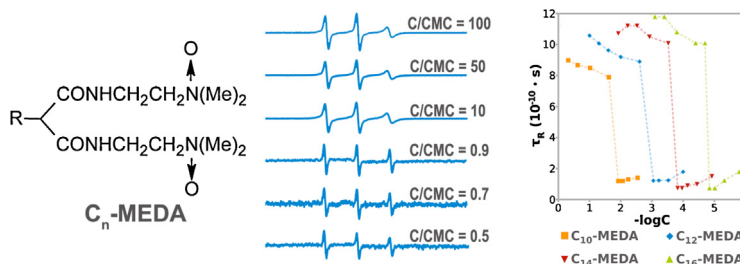
<sup>a</sup> Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

<sup>b</sup> Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

### HIGHLIGHTS

- Alkylamide di-N-oxide derivatives represent a new class of dicephalic amphoteric surfactants exhibiting profound surface properties.
- Aggregation behavior of C<sub>n</sub>-MEDA's at free surface or in bulk at physiological pH was studied by means of interfacial tensiometry, EPR and DLS.
- Structural properties of C<sub>n</sub>-MEDA's were performed on the theoretical basis by employing in silico techniques (DFT and QSAR).

### GRAPHICAL ABSTRACT



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### ABSTRACT

A series of dicephalic-type 1,1-bis{[3-(N,N-dimethylamino) ethyl]amido}alkane-di-N-oxide surfactants were synthesized and their aggregation behavior in an aqueous environment was described, both experimentally and theoretically. Surface tension and electron paramagnetic resonance (EPR) spectroscopy were applied to monitor the micellization behavior of the studied dicephalic surfactants in aqueous solutions. In the EPR experiments two nitroxide spin probes (5- and 16-doxylstearic acids) were used whereby not only the critical micelle concentrations could be determined, but also the microenvironment of the formed aggregates could be investigated as a function of temperature and surfactant concentration. Furthermore, the size of the micellar aggregates and the polydispersity indexes of the micellar solutions were established by dynamic light scattering (DLS). The structures of the formed aggregates, defined by the critical packing parameter, were predicted using the QSAR approach. The hydrodynamic radii, micellar volumes and aggregation numbers were computed with the long range corrected B3LYP hybrid functional (CAM-B3LYP). In order to put the results obtained for the dicephalics into perspective the experiments and computations were performed for the standard 2-(dodecanoylamino)ethyl dimethylamine-N-oxide.

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### 1. Introduction

Rearrangement through the self-aggregation of surfactants in a solution and at the interfaces has long been a matter of extensive interest to scientists. Thanks to the availability of a variety

of physicochemical methods, such as: tensiometry, neutron scattering, dynamic light scattering, electron spin resonance, nuclear magnetic resonance, conductance, microcalorimetry, ellipsometry and fluorescence spectroscopy, it has become possible to describe many micellar solutions from the point of view of their thermodynamic and/or kinetic parameters [1–5]. It is important to control the morphological and structural characteristics of many self-organized surfactant systems in order to obtain both a variety of classical performance properties (e.g. wetting and foaming

\* Corresponding author. Tel.: +48 71 3202828; fax: +48 71 3203678.

E-mail address: [kazimiera.wilk@pwr.wroc.pl](mailto:kazimiera.wilk@pwr.wroc.pl) (K.A. Wilk).

ability, solubilization, detergency) and new desired features (e.g. engineering surfaces and nanostructures, encapsulation and reaction media, models for membranes) [1,6–8]. Among a variety of environmentally friendly surfactants (the so-called soft surfactants), N-oxide structures have received much attention because of their pH-sensitive aggregation behavior, improved performance (e.g. emulsifying ability, low irritant action, gelating and antioxidative properties), better biodegradability and lower toxicity [9–13]. They are widely used commercially as foaming and wetting agents and thickeners in shampoo formulas, hair conditioners, body care as well as in dish and laundry detergents and fabric softeners [9]. Generally, N-oxide surfactants are easily prepared by oxidizing tertiary amine compounds with aqueous hydrogen peroxide in an aqueous or aqueous-alcoholic medium. Furthermore, it has recently been found that through even slight modifications of the molecular structure of amine oxide type surfactants, e.g. by inserting a weak bond (the so-called 'labile') into the hydrophobic N-oxide backbone or/and by introducing hydrophilic or hydrophobic entities into the surfactant structure, one may achieve high quality products with multifunctional capabilities [14–16].

In our recent papers we described the preparation and surface properties of 2-(alkanoylamino)ethyl dimethylamine-N-oxides having a single-chain and single-head structure [15,17], and of the so-called dicephalic *N,N*-bis(3,3'-(dimethylamino)propyl)alkylamide di-N-oxides comprising one hydrophobic tail and two hydrophilic entities linked by a connector to a nitrogen bridge [16]. As the continuation of the studies of ecologically safe products [15–18], a new family of dicephalic 1,1-bis{[3-(*N,N*-dimethylamino) ethyl]amido}alkane-di-N-oxides (for the structures and abbreviations see Chart 1) was synthesized and characterized with regard to the effect of changes in the molecular structure and in the environment around the dicephalic surfactants on their self-aggregation behavior in an aqueous solution at the physiological pH. Chart 1 shows that the studied surfactants provide a homologous series of single tail-double head structures with both hydrophilic entities being grafted by the amide labile bond.

In the present contribution we aimed to describe the aggregation behavior of  $C_n$ -MEDA derivatives by means of interfacial tensiometry, electron paramagnetic resonance (EPR) spin probe technique and dynamic light scattering (DLS). The concentrations of the nonionic  $C_n$ -MEDA form at a pH close to physiological ( $\sim 7$ ) was evaluated potentiometrically. In all the performed experiments 2-(dodecanoylamino)ethyl dimethylamine-N-oxide was treated as a standard surfactant. As regards the EPR measurements, 5- and 16-doxylstearic acids (respectively denoted as 5-DSA and 16-DSA in Chart 1) were used as spin probes, whereby critical micelle concentration (CMC) values and the microviscosity and local polarity of the  $C_n$ -MEDA micelles could be determined. The further analysis of the structural properties was carried out on the theoretical basis by employing *in silico* techniques (DFT and QSAR). The obtained results will be useful in the targeted design of bifunctional N-oxide surfactants to be used in a variety of modern consumer products. Owing to their structural features, the surfactants are expected to exhibit beneficial self-organization behavior, high performance properties and environmental acceptance.

## 2. Experimental

### 2.1. Materials

Dicephalic 1,1-bis{[3-(*N,N*-dimethylamino) ethyl]amido}alkane-di-N-oxides ( $C_n$ -MEDA) were synthesized according to the directions given in [14]. An equimolar mixture of diethyl 2-hexadecylmalonate and *N,N*-dimethylethylenediamine was stirred and heated at 120–130 °C for two days under

nitrogen. The unreacted diamine was evaporated under reduced pressure. The crude reaction product–1,1-bis{[3-(*N,N*-dimethylamino)ethyl]amido}alkane–was purified through repeated crystallization from hexane. Then 30 wt.% of aqueous hydrogen peroxide was added dropwise over an hour to the amine dissolved in propanol-2 at 333 K. After cooling to room temperature all the volatile substances were evaporated under reduced pressure. The solid residue was dried and then purified through repeated crystallization from chloroform. The  $C_n$ -MEDA series do not exhibit Krafft points in the temperature range of 277–373 K. Spectroscopic and analytical data for  $C_{12}$ -MEDA are presented as follows;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{CH}-$  0.85 (t, 3H,  $^3J_{\text{HH}} = 6.5$  Hz);  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{CH}-$  1.23–1.35 (m, 20 H);  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{CH}-$  1.82–1.87 (m, 2H);  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{CH}-$  3.26 (t, 1H  $J_{\text{HH}} = 7.5$  Hz);  $-\text{CONH}$  8.57 (m, 2H);  $-\text{CONHCH}_2\text{CH}_2\text{N}$  3.37–3.47 (m, 4H);  $-\text{CONHCH}_2\text{CH}_2\text{N}$  3.82 (t, 4H  $J_{\text{HH}} = 6.7$  Hz);  $-\text{N}(\text{CH}_3)_2$  3.25 (s, 12H). Elemental analyses were carried out using a Vario EL III CHNS analyzer. Calculated: C: 62.13%; H: 10.88%; N: 12.60%; found: C: 62.16%; H: 10.86%; N: 12.57%. Electrospray ionization (ESI) spectra were obtained using a MicroTOF-Q mass spectrometer. The ESI-MS (MH<sup>+</sup>) result for  $C_{12}$ -MEDA amounted to 445.4. The chemical stability of the  $C_n$ -MEDA aqueous solutions was proved by  $^1\text{H NMR}$  spectroscopy (solutions in  $\text{D}_2\text{O}$ , TSP as the standard). The  $^1\text{H NMR}$  spectra taken at weekly intervals during the month of storage indicated no signals shift relative to the TSP.

2-(dodecanoylamino)ethyl dimethylamine-N-oxide ( $C_{12}$ -EDA) was synthesized and purified strictly according to the directions given in [19]. An elemental analysis and  $^1\text{H NMR}$  spectra proved its purity and its chemical structures were revealed by the spectroscopic and analytical data:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{CH}_2-$  0.84 (t, 3H,  $^3J_{\text{HH}} = 6.51$  Hz);  $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{CH}_2-$  1.20–1.32 (m, 16H);  $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{CH}_2-$  1.52–1.57 (m, 2H);  $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{CH}_2-$  2.24 (t, 2H);  $-\text{CONH}$  7.96 (bd, 1H);  $-\text{CONHCH}_2\text{CH}_2\text{N}$  3.78 (q, 2H);  $-\text{CONHCH}_2\text{CH}_2\text{N}$  3.61 (t, 2H);  $-\text{N}(\text{CH}_3)_2$  2.67 (s, 6H) (s, bd, t, and m, denotes singlet, broad doublet, triplet, and multiplet, respectively). Electrospray ionization (ESI) spectra were obtained using a MicroTOF-Q mass spectrometer. The ESI-MS (MH<sup>+</sup>) result for  $C_{12}$ -EDA amounted to 287.6.

The two spin probes, i.e. 5-doxylstearic acid (5-DSA) and 16-doxylstearic acid (16-DSA), used in the EPR experiments (Chart 1) were purchased from Aldrich Chemical Co. (Milwaukee, WI) while the hydrogen peroxide (30% solution) was purchased from POCH (Gliwice). The other reagents and solvents were of commercial grade and were not additionally purified before use. The water used in all the experiments was doubly distilled and purified by means of a Millipore Milli-Q purification system (Bedford, MA).

### 2.2. Surface tension measurements

Surface tension measurements were performed at  $295 \pm 0.1$  K using a Krüss K12 microprocessor tensiometer (Krüss, Hamburg, Germany) equipped with a du Nouy Pt-Ir ring (resolution  $\pm 0.01$  mN/m). The experiments were conducted in the same manner as in our recent paper [16]. The surface tension data were reproducible within  $\pm 0.2$  mN m<sup>-1</sup>. From the obtained data critical micelle concentration (CMC) values were extracted [14,16,19].

### 2.3. Potentiometric measurements

Equilibrium constants for the protonation of the N-oxide groups were determined by pH-potentiometric titrations of 1.5 cm<sup>3</sup> samples of surfactant solutions in HCl ( $C = 4$  mM,  $I = 0.1$  M). The electrode system was calibrated each day by titrating the HCl solution ( $C = 4$  mM,  $I = 0.1$ ) against the standard NaOH solution. The resulting titration data were used to calculate the standard electrode potentials. The value of  $\text{p}K_w = 13.77$  was used as the dissociation

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