



SURFACE PROPERTIES OF SILOXANE-BASED SURFACTANTS CONTAINING TROMETHAMOL UNITS

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New siloxane-based amphiphilic compounds: a dimer and two copolymers with pendant functional groups have been synthesized starting from tris(hydroxymethyl)aminomethane (tromethamol) and glycidyl-functionalized siloxane precursors. These new compounds were designed as an alternative to carbohydrate-modified siloxane surfactants, which are more difficult to obtain. The water soluble compounds (a dimer and a copolymer with 1.5/1 dimethyl/ hydrophilic group ratio) exhibited typical surfactant behavior. Low CMC values and equilibrium surface tensions were detected by tensiometry. Very good wetting behavior towards glass and silicone elastomer was observed by dynamic contact angle measurements. Due to their structure, these surfactants could be used for improving surface properties of contact lenses. Preliminary tests showed good coverage of the surface and transparency. Dynamic vapor sorption (DVS) experiments showed improved dehydration behavior of the treated material.

INTRODUCTION

Siloxane moieties are used as hydrophobic parts in surfactants with various structures. The uniqueness of these surfactants is their solubility both in water and in organic solvents; the siloxane units are responsible for reducing the surface tension and for hydrophobic as well as oleophobic properties. Siloxane surfactants usually have low CMC values and thus are required in small amounts. The reasons for this unique behavior are the high flexibility and low cohesive energy of the siloxane bond.^{1,2} Polydimethylsiloxanes (PDMS) have very low glass transition temperature, transparency to visible and UV light, high permeability to various gases (especially oxygen), physiological inertness, excellent blood compatibility (low interaction with plasma proteins).³ The most commonly known siloxane surfactants contain hydrophilic polyoxyalkylenes (polyether) portions.⁴ The combination of carbohydrates and silicones has also received great attention in both scientific and economic media,⁵⁻⁹ especially due to their excellent biodegradability, good dermatological compatibility, and absence of toxic effects.

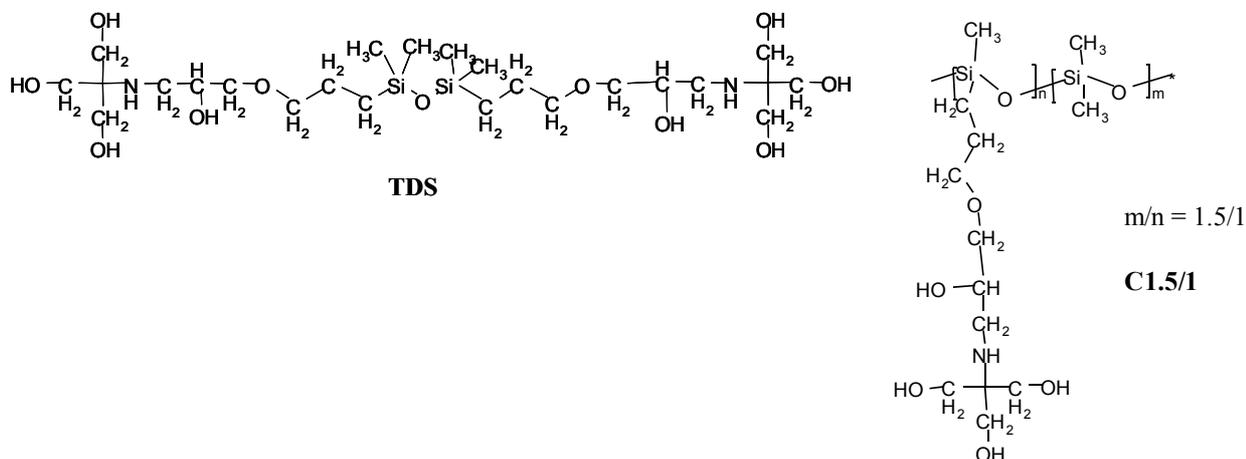
As an alternative to carbohydrate-siloxane surfactants, we propose a new class of surfactants, which are easier to synthesize, being at the same time biocompatible by structure. In these surfactants, tris(hydroxy-methyl)aminomethane (known as tromethamol, Tris or THAM) is used as partner for polysiloxanes. The synthesis of a disiloxane and two siloxane copolymers containing THAM units was recently described.¹⁰ The resulting compounds exhibited very good surface properties and could be valuable candidates for medical or cosmetic use, given the biocompatibility of the starting constituents. In this paper we focus on wetting behavior of these surfactants and we describe preliminary tests for modification of surface properties of silicone-based materials after treatment with these compounds. Promising results have been obtained, that would recommend such surfactants as environmental friendly detergents or components for improved performance in contact lenses, although this aspect remains to be studied thoroughly.

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RESULTS AND DISCUSSION

THAM-modified siloxane compounds were synthesized according to ref. 10. The main reaction was an addition between the primary amine group in THAM and the cyclic ether group in

glycidyloxypropyl-siloxanes. The facile synthesis, in mild conditions is an advantage compared to the carbohydrate-modified siloxanes. In the present work, we used a disiloxane (TDS) and a water-soluble copolymer (C1.5/1), with structures described in Scheme 1.



Scheme 1 – Chemical structure of the studied surfactants.

The modified siloxane compounds were characterized by IR and $^1\text{H-NMR}$. In the IR spectra a new absorption band was observed at 1657 cm^{-1} in the copolymer and at 1654 cm^{-1} in the disiloxane, which is due to the secondary amine group, instead of the band at 1589 cm^{-1} , corresponding to the primary amine in THAM. The disappearance of the bands characteristic to the glycidyl groups in the reagents, at 3052 , 1159 and 910 cm^{-1} also confirmed the reaction. In the $^1\text{H-NMR}$ spectra, besides the presence of all the expected protons, the correct integral ratio confirmed the reaction and the purity of the obtained compound. The CMC values were determined by tensiometry, using Wilhelmy plate method, at 22°C . A typical surfactant behavior was observed in water for TDS and C1.5/1. In a $\gamma - \log(\text{conc})$ plot, CMC values were determined, using the adequate software. CMC of 66.5 and 45 mg/L for TDS and C1.5/1 respectively were found.

The dynamic contact angles of glass slides against diluted surfactant solutions were determined using the tensiometer. The values of advancing contact angle (θ_{adv}) for TDS (54.5°) and for C1.5/1 (44°) were lower than those obtained for pure water and for Pluronic F68. The receding contact angle was 0° in both cases, which signifies a complete wetting of the glass.

In order to test the wetting behavior on a hydrophobic surface, we used as a reference a silicone elastomer (SE) prepared in our laboratory (polydimethylsiloxane- α,ω -diol reinforced with 13.2% silica by sol-gel technique). We measured the dynamic contact angle of the silicone material against water and a 0.4g/L surfactant solution, respectively. The results are presented in Table 1. Low advancing and 0° receding contact angle indicate a very good wetting of this hydrophobic material.

Table 1

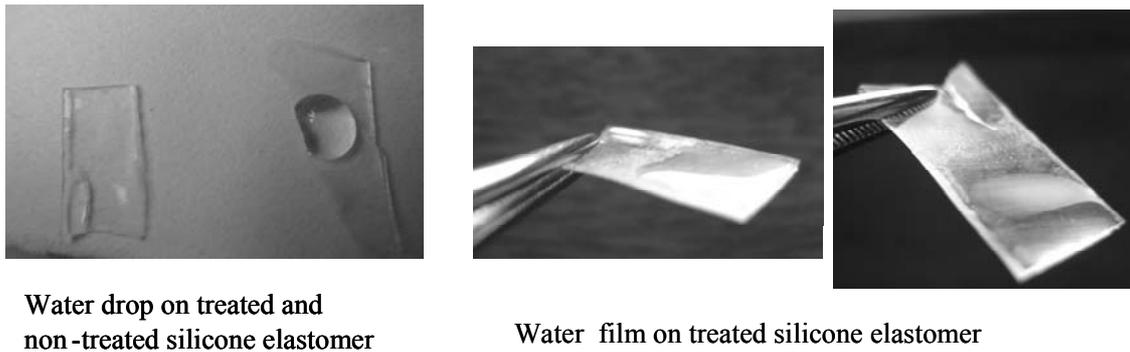
Dynamic contact angles (measured by Wilhelmy plate method) on un-treated silicone elastomer (SE) and on the same material after treatment with C1.5/1 and TDS

	Solid probe / measuring liquid	First advancing contact angle ($^\circ$)	First receding contact angle ($^\circ$)	Second advancing contact angle ($^\circ$)
1.	Un-treated SE / water	107.5	83.5	109
2.	Un-treated SE / solution of C1.5/1	52	0	35
3.	SE treated with C _{1.5/1} / water	78	53	62
4.	SE treated with TDS/ water	90	68	88

In another experiment, a piece of silicone elastomer was incubated in diluted surfactant solutions then the dynamic contact angle against water was measured. As can be observed (Table 1) significant decrease of both advancing and receding contact angles compared to un-treated material was obtained by this surface treatment. The very good wetting of SE surface can be visually assessed by spreading a drop of water on a

silicone elastomer treated with surfactant solution (Fig. 1).

In order to test the transparency of surfactant coatings, glass slides were analyzed by spectrophotometry after different treatment with the two surfactants (Fig. 2). The result showed over 97% visible light transmission, taking the neat glass as a reference.



Water drop on treated and non-treated silicone elastomer

Water film on treated silicone elastomer

Fig. 1 – Wetting behavior of a silicone elastomer treated with a 0.4g/L solution of C1.5/1.

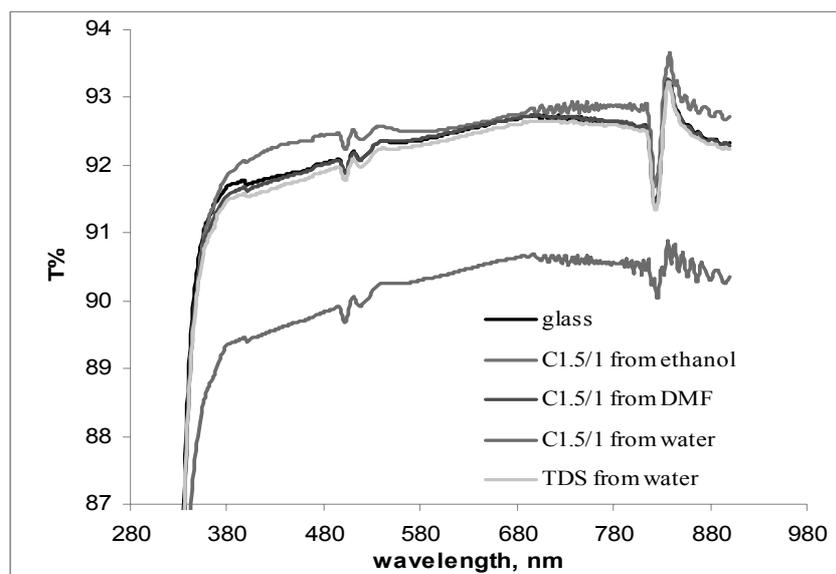


Fig. 2 – UV-Vis transparency of surfactant coatings on glass slides.

Due to the structural biocompatibility, siloxane surfactants with tromethamol units could have various biomedical applications. We started to investigate the surface modifications that such a surfactant could bring to contact lenses. One reason is that tromethamol derivatives are used in the treatment of allergic conjunctivitis and in the prevention and treatment of postoperative inflammation. Another motivation is that the multiple OH groups would improve the behavior towards water of siloxane-containing contact

lenses. Additionally, the siloxane backbone is important for a good compatibility and adsorption on the surface of silicone-based hydrogel contact lenses.

In Fig. 3, AFM images of a worn contact lens before and after treatment with an aqueous solution of C1.5/1 are presented. The effect of the surface treatment, as revealed by phase analysis, was homogeneous over the scanned area; no clusters or different phase material were observed.

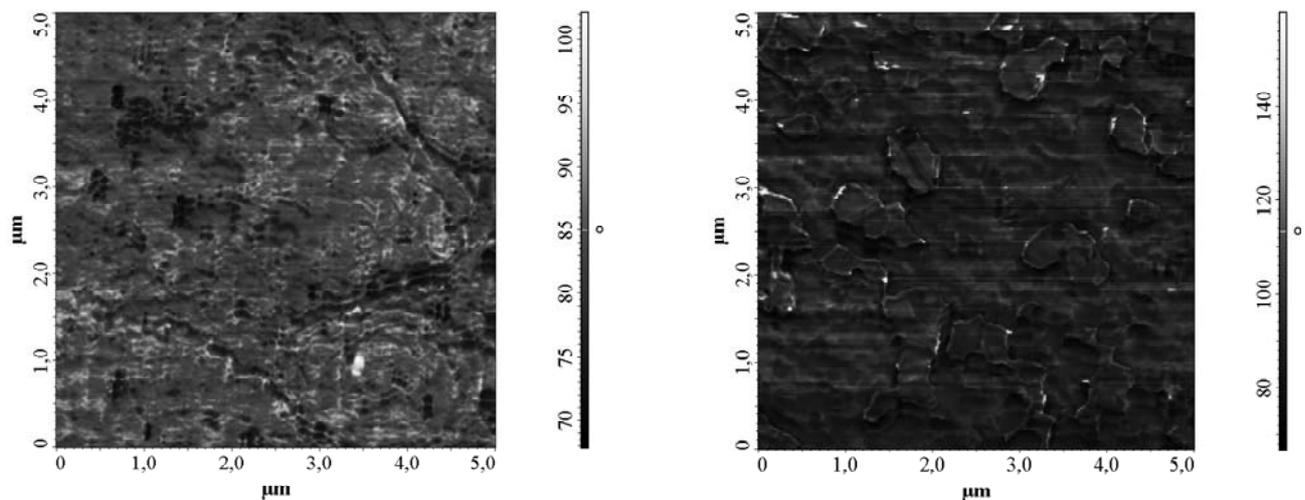


Fig. 3 – AFM (phase) images for a used silicone hydrogel contact lens: before (left) and after treatment with C1.5/1 (right).

In order to investigate the modification of wetting and dehydration behavior, a silicone hydrogel contact lens was treated with aqueous or ethanolic solution of C1.5/1 for 24h and the dynamic vapor sorption (DVS) curves were registered at 25°C. The material was firstly dried at constant weight in flowing nitrogen at RH<1%. Then the relative humidity (RH) was increased from 0 to 90% in 10% humidity steps, and the sorption equilibrium was obtained in each step. Subsequently, the RH decreased in a similar way and the desorption curves were registered. The

moisture sorption-desorption isotherms are presented in Fig. 4. All the obtained curves have similar shapes, indicating type III isotherms, according to IUPAC classification.¹¹ This type is characteristic for low hydrophilic materials with weak sorbent-water interactions. Such materials have low sorption at low humidities, moderate sorption at middle relative humidities and suddenly high water sorption at humidities in close proximity of 100%.

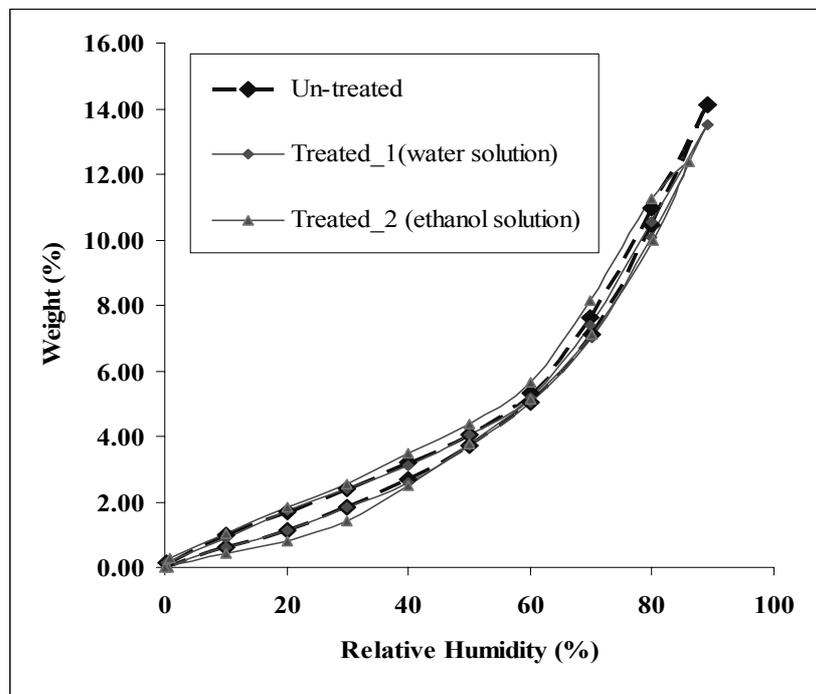


Fig. 4 – Moisture sorption-desorption isotherms for the lens samples.

As can be observed (Fig. 4 and Table 2), the water uptake at maximum RH decreased in the materials treated with aqueous and especially with ethanolic solution of the siloxane surfactant. It was established that lower water content is effective at keeping bacteria from adhering to the lens surface.¹²

In another experiment, after reaching the sorption equilibrium at RH=90%, the tested materials have been maintained at RH=40% for 1h, in order to register the dehydration curves at constant RH. As can be observed from Table 2, the percent of water eliminated in these conditions decreased slightly in the contact lens treated with

aqueous solution of C1.5/1 and showed a more significant decrease in the case of ethanol solution. If we report the water loss values to the reference material (un-treated), we obtain a 8.6 % improvement of the dehydration resistance for C1.5/1 in ethanol.

Based on these preliminary results, it seems that surface treatment of silicone hydrogel with a THAM modified polysiloxane can determine diminished dehydration and thus, could improve comfort and enhance the wearing time of the contact lenses. Further investigations are in progress.

Table 2

DVS results for contact lens hydrogel treated with C1.5/1, at 25°C

Sample	% adsorbed water (RH=0-90%)	% water eliminated after 60 min at RH=40% (W*)	% Improvement of dehydration resistance (D**)
Un-treated	14.1183	12.2617	-
Treated_1 (water solution)	13.4952	12.0275	1.91
Treated_2 (ethanol solution)	12.3542	11.2065	8.61

$$* W = \frac{mass_{90\%} - mass_{40\%}}{mass_{90\%}} \cdot 100 = \text{water_loss} = \text{dehydration}$$

$$** D = \frac{W_{un-treated} - W_{treated}}{W_{un-treated}} \cdot 100$$

EXPERIMENTAL

Materials. A dimmer and a copolymer with pendant tromethamol groups have been synthesized starting from tris(hydroxymethyl)aminomethane (tromethamol) and glycidyl-functionalized siloxane precursors, in the presence of isopropyl alcohol. The preparation details have been recently described.¹⁰ Double-distilled water and high purity solvents were used for surface tension measurements and surface treatment.

Measurements. The infrared spectra were registered on a Bruker Vertex 70 FT-IR instrument. ¹H-NMR spectra were registered on 400 MHz Bruker spectrometer in D₂O or CDCl₃ without internal standard. Surface tension, critical micelle concentration (CMC) and dynamic contact angle were measured with an automatic tensiometer, Sigma 700 from KSV, using the Wilhelmy plate method, adequate software and external dosing for CMC detection. The AFM measurements were made on a SPM Solver Pro-M platform (NT-MDT, Rusia), in air, in semi-contact mode. The transparency was measured using a Specord M42 spectrophotometer, at ambient temperature. Water vapor sorption capacity of the samples has been measured by using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK).

CONCLUSIONS

The surface properties of a tromethamol-modified disiloxane and a siloxane copolymer have

been investigated. Good wetting behavior towards hydrophilic (glass) and hydrophobic (PDMS) materials has been found. Silicone hydrogel contact lens exhibited improved dehydration resistance after treatment with diluted solutions of a tromethamol-polysiloxane.

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