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# Silicon-modified Surfactants and Wetting: I. Synthesis of the Single Components of Silwet L77 and Their Spreading Performance on a Low-energy Solid Surface†

R. Wagner,[1]* Y. Wu,[1] G. Czichocki,[1] H. v. Berlepsch,[1] B. Weiland,[1] F. Rexin[1] and L. Perepelittchenko[2]
[1]Max-Planck-Institute for Colloids and Surfaces, Rudower Chaussee 5, 12489 Berlin, Germany
[2]Institute for Petrochemical Synthesis, Leninskii Prospekt 29, 117912 Moscow, Russia

**Defined surfactants of general formula $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_{3-9}OCH_3$, have been synthesized from the corresponding oligoethylene glycol monoallyl monomethyl ethers via hydrosilylation. The concentration-dependent spreading performance on hydrophobized silicon wafers has been investigated and compared with that of Silwet L77. For the hexaethylene glycol derivative the highest initial spreading velocities and largest spreading areas were found. Since Silwet L77 spreads faster than all the other derivatives under investigation, a synergistic effect of different compounds is unlikely. Minor differences were found for handshaken and sonicated solutions. Copyright © 1999 John Wiley & Sons, Ltd.**

**Keywords: surfactants; silicon-modified; wetting; spreading behaviour**

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## 1 INTRODUCTION

Aqueous solutions of certain trisiloxane surfactants rapidly wet low-energy surfaces (water contact angle >90°).[1] The spreading rate of a 'superspreader' solution significantly exceeds that expected for a process controlled purely by liquid diffusion.[2,3]

It has been shown recently that this unique property is part of the much broader concept of a surfactant-enhanced spreading. Aqueous solutions of ethoxylated alcohols ($C_iE_j$) rapidly wet moderately hydrophobic solid surfaces.[4,5] The same effect was observed for certain double-chained anionic and cationic hydrocarbon surfactants.[6] A detailed analysis of spreading data obtained at a silicon-surfactant solution/liquid hydrocarbon interface led to the conclusion that this rapid spreading can be understood as a Marangoni flow-driven process.[7] Although the role of dispersed surfactant phases[4,5] or microstructures has been demonstrated, a clear cut correlation between spreading performance and extensively studied phase behaviour[8–10] could not be established.

Even less understood is the evolution of the liquid/vapour interfacial energies ($\gamma_{lv}$) and solid/liquid ($\gamma_{sl}$) under spreading conditions. Since interfacial energies reflect the collective (macroscopic) behaviour of molecules at interfaces, a quantitative description could improve the understanding for the underlying mechanisms considerably. Unfortunately, easily accessible dynamic liquid/liquid interfacial tension measurements[11] can hardly be substitute for experiments at the solid/liquid interface. A promising approach has recently been published by Chaudhury.[12] He studied the dynamic adsorption of hydrocarbon-based surfactants to a PDMS sheet/PDMS half-sphere system. Alternatively we developed a modified Wilhelmy method. In separate runs, geometrically identical V2A steel plates (completely wettable, $\gamma_{lv}$) and FEP® plates (not completely wettable, $\gamma_{sl}$) are immersed in a given surfactant solution. Dynamic contact angles as well as the Lifshitz–van der Waals and donor–acceptor con-

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* Correspondence to: R. Wagner, Max-Planck-Institute for Colloids and Surfaces, Rudower Chaussee 5, 12489 Berlin, Germany.

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tributions of both interfacial energies can be determined (Ref. 13 see also R. Wagner, L. Richter and S. Siegel, *Acta Physicochem. Sinica*, in press)

Despite the numerous efforts described above, apparently simple questions concerning the rapid spreading of siloxane surfactants on low-energy surfaces remained unsolved. Which single components of the complex surfactant mixtures are responsible for the superspreading effect? Does a synergistic effect exist? Do siloxane surfactants of distinctly different spreading performance differ with respect to the evolution of their dynamic liquid/vapour and solid/liquid interfacial energies. Can the microscopic shapes of the leading edges of rapidly spreading drops be visualized? Does the microscopic drop shape depend on the spreading velocity?

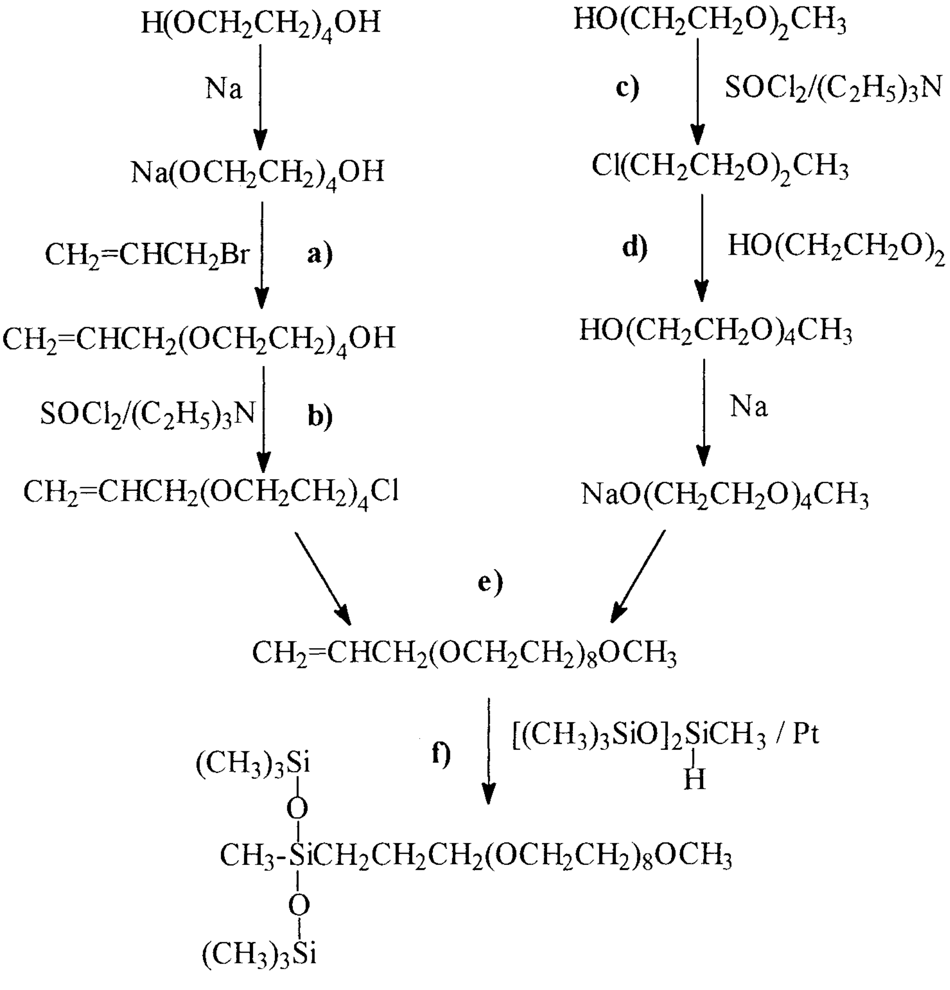
Therefore, it is an objective of this paper to describe the synthesis of the single components of the intensively investigated superspreader Silwet L77® (Union Carbide). Further, the concentration-dependent spreading performance of these well-defined molecules is investigated and compared with that of Silwet L77®.

# 2 MATERIALS AND METHODS

## 2.1 Materials

### 2.1.1 Heptamethyltrisiloxanyl derivatives of oligoethylene glycols

In order to synthesize defined 1,1,1,3,5,5,5-hepta-



**Scheme 1** Reaction sequence yielding the octaethylene glycol derivative of 1,1,1,3,5,5,5-heptamethyltrisiloxane.

**Table 1** Chain lengths and boiling points of key intermediates

| $HO(CH_2CH_2O)_r$ $CH_2CH{=}CH_2$ $r$ (B.p., °C/mmHg) | $Cl(CH_2CH_2O)_r$ $CH_2CH{=}CH_2$ $r$ (B.p., °C/mmHg) | $Cl(CH_2CH_2O)_sCH_3$ $s$ (B.p., °C/mmHg) | $HO(CH_2$ $CH_2O)_{s+t}CH_3$ $s+t$ (B.p., °C/mmHg) | $r+s+t$ |
|---|---|---|---|---|
| 2 (218–224/760) | 2 (202–210/760) | | 1 (124/760)[a] | 3 |
| 1 (158–162/760) | 1 (134–138/760) | | 3 (122/10)[a] | 4 |
| 2 | 2 | | 3 | 5 |
| 4 (128–138/0.5) | 4 (117–128/1) | | 2 (194/760)[a] | 6 |
| 4 | 4 | | 3 | 7 |
| 4 | 4 | 2 (164–174/760) | 4 (112–118/0.3) | 8 |
| 4 | 4 | 2 | 5 (148–153/0.5) | 9 |

[a] Commercially available (Aldrich).

methyltrisiloxanyl (MD*M) derivatives of general formula $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_{3–9}$ $OCH_3$ a complex reaction sequence was applied (Scheme 1).

Key intermediates for the final hydrosilylations (f) are the oligoethylene glycol monoallyl monomethyl ethers. They have been synthesized from monochloro oligoethylene glycol monoallyl ethers and monomethyl ethers of oligoethylene glycols via the Williamson synthesis (e). Since most compounds of both starting material types are not commercially available, they had to be built up from low-molecular-weight precursors via the Williamson-type etherifications (a) and (d) as well as chlorinations (b) and (c).[14,15]

In Table 1 the general structures of key intermediates and the chain lengths of the desired oligoethylene glycol moieties are summarized. The number of ethylene glycol moieties incorporated via allyioxy derivatives is denoted with $r$. The letters $s$ and $t$ describe the number of ethylene glycol moieties which were attached to the methoxy side during the synthetic procedure.

Table 2 summarizes the structures and the boiling points of the allyl and siloxanyl derivatives of defined oligoethylene glycols.

Table 3 summarizes the isolated yields colours, purities and product compositions of the siloxanyl-modified oligoethylene glycols, Capillary GC–MS experiments were used to identify the chemical nature of the contamination. The occurrence of intensive peaks at $m/z = 221$, 215 and 73 (heptamethyltrisiloxanyl, hexamethyltrisiloxanyl, trimethylsilyl) indicated siloxanyl moieties. For silicon-free impurities (typically oligoethylene glycols), strong signals at $m/z = 59$ and 103 ($OCH_2CH_2O - H$, $OCH_2CH_2OCH_2CH_2O - H$) were found. The retention times of the silicon-containing contamination gave access to their probable chemical structure. For these impurities retention times close to those of the synthesized derivatives (deviation <10%) were found.

Table 4 contains the structure-confirming 13C-NMR signals for derivative $EO_3$.

### 2.1.2 $(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_8$ $OCH_3$ ($EO_8$)

*Procedure (a)*

Tetraethylene glycol (1532 g; 8 mol) was placed under argon in a three-necked bottle equipped with refluxing condenser and magnetic stirrer. The temperature was raised to 140 °C and 57.5 g (2.5 mol) sodium was added over 2 h. Due to the exothermic reaction the temperature rose to 170 °C. Allyl bromide (307 g; 2.5 mol) was placed under argon in a second three-necked bottle equipped with refluxing condenser, argon inlet and mechanical stirrer. The hot glycolate was transferred into this water-cooled bottle over 30 min and NaCl immediately started to precipitate. Afterwards the mixture was heated to 170 °C for 1 h. The NaCl was filtered off and 10 g $NaHCO_3$ was added. After repeated filtration the mixture was distilled three times over a Vigreux column. The final distillation was carried out over a 50 cm packed column. A pale yellow oil (390 g; b.p. 128–138 °C/0.5 mmHg) was obtained. GC analysis showed it to consist of tetraethylene glycol monoallyl ether (75%), tetraethylene glycol diallyl ether (10%) and tetraethylene glycol (15%).

*Procedure (b)*

Tetraethylene glycol monoallyl ether (372 g; 1.58 mol) and 191 g (1.9 mol) triethylamine were placed in a four-necked bottle equipped with refluxing condenser, dropping funnel, mechanical

**Table 2** Boiling points of allyl and siloxanyl derivatives of defined oligoethylene glycols

| $CH_3O(CH_2CH_2O)_{r+s+t}CH_2CH{=}CH_2$ (B.p., °C/mmHg) | $CH_3O(CH_2CH_2O)_{r+s+t}(CH_2)SiCH_3[OSi(CH_3)_3]_2$ (B.p., °C/mmHg) | Abbrev. |
|---|---|---|
| 3 (80–83/0.35) | 3 (136–140/0.35) | $EO_3$ |
| 4 (128–130/0.5) | 4 (167–173/0.3) | $EO_4$ |
| 5 (154–156/0.2) | 5 (187–195/0.3) | $EO_5$ |
| 6 (174–178/0.2) | 6 (216–226/0.7) | $EO_6$ |
| 7 (194–200/0.5) | 7 (237–242/0.7) | $EO_7$ |
| 8 (235–240/1) | 8 (249–256/0.75) | $EO_8$ |
| 9 (255–263/1) | 9 (272–281/0.75) | $EO_9$ |

stirrer and argon inlet. After cooling to 0 °C, 216 g (1.9 mol) thionyl chloride was added over 1 h. The mixture turned black and the temperature rose to 70 °C. The reaction product (a black cake) was cooled to room temperature, liquefied by addition of diethyl ether and filtered. The $(C_2H_5)_3N{\cdot}HCl$ obtained was washed several times with diethyl ether. The ether fractions were combined and over 10 min a black viscous oil precipitated from the solution. Repeated vacuum distillations yielded 178 g of a pale yellow liquid (b.p. 117–128 °C/1 mmHg). It contained monochloro tetraethylene glycol monoallyl ether (72%), tetraethylene glycol diallyl ether (16%) and dichloro tetraethylene glycol (12%).

### *Procedure (c)*

The method described under procedure (b) was used to react 540 g (4.5 mol) diethylene glycol monomethyl ether, 505 g (5 mol) triethylamine and 596 g (5 mol) thionyl chloride. Distillation under atmospheric pressure yielded 234 g monochloro diethylene glycol monomethyl ether (colourless oil, b.p. 164–174 °C purity 96%).

### *Procedure (d)*

The method described under procedure (a) was used to react 716 g (6.75 mol) diethylene glycol and 38.8 g (1.6 mol) sodium. During the sodium addition the temperature rose from 100 °C to 170 °C. The hot glycolate was transferred to a separate bottle which contained 234 g (1.69 mol) monochloro diethylene glycol monomethyl ether. The temperature was raised to 170 °C for 1 h. After filtration and distillation 134 g tetraethylene glycol monomethyl ether (colourless oil, b.p. 113–118 °C/0.3 mmHg, purity 98%) was obtained.

### *Procedure (e)*

In analogy to (a), 134 g (0.65 mol) tetraethylene glycol monomethyl ether was placed in a three-necked bottle and heated to 180 °C. The addition of 9.2 g (0.4 mol) sodium increased the temperature to 200 °C. The hot glycolate was transferred into a separate bottle which contained 101 g (0.4 mol) monochloro tetraethylene glycol monoallyl ether. The mixture was heated to 170 °C for 1 h. After filtration the product was distilled five times in vacuum (15 cm Vigreux column). The

**Table 3** Hydrosilylation yields, colours and purities of the siloxanyl-modified oligoethylene glycols, contamination compositions and average particle sizes of 0.01% aqueous solutions

| | Yield (%) | Colour | Purity (%GC) | Contamination (%) Si | Contamination (%) Without Si | Particle size in 0.01% solution (nm) |
|---|---|---|---|---|---|---|
| $EO_3$ | 62 | Colourless | $\gg 99$ | | | 1081 |
| $EO_4$ | 44 | Colourless | $\gg 99$ | | | 1104 |
| $EO_5$ | 32 | Colourless | 99 | | 1 | 376 |
| $EO_6$ | 28 | Pale yellow | 97.5 | 1 ($EO_5$ type) | 1.5 | 353 (us); 380 (hs)[a] |
| $EO_7$ | 55 | Pale yellow | 96 | 1.5 ($EO_6$ type) | 2.5 | 254 |
| $EO_8$ | 33 | Yellow | 95 | 1.5 ($EO_6$ type) | 3.5 | 159 |
| $EO_9$ | 24 | Pale brown (Pt) | 90 | 10 ($EO_7 + EO_8$ type) | | 144 |

[a] us, ultrasonication; hs, handshaken.

**Table 4** $^{13}$C NMR shifts of selected substructures of derivative $EO_3$

| Substructure | $(\mathit{C}\mathrm{H}_3)_3\mathrm{Si}$ | $\mathit{C}\mathrm{H}_3\mathrm{Si}$ | $\mathrm{Si}\mathit{C}\mathrm{H}_2$ | $\mathrm{SiCH}_2\mathit{C}\mathrm{H}_2$ | $\mathrm{SiCH}_2\mathrm{CH}_2\mathit{C}\mathrm{H}_2$ | $\mathrm{O}\mathit{C}\mathrm{H}_3$ |
|---|---|---|---|---|---|---|
| shift (ppm) | 1.75 | −0.49 | 13.41 | 23.10 | 74.00 | 58.91 |

octaethylene glycol derivative (15 g pale yellow oil, b.p. 235–240 °C/1 mmHg, purity 95%) was obtained.

*Procedure (f)*
Octaethylene glycol monoallyl monomethyl ether (7.8 g; $1.83 \times 10^{-2}$ mol) 8.16 g ($3.61 \times 10^{-2}$ mol) $M_2D^H$ and 12 mg ($1.83 \times 10^{-6}$ mol) of a 3% Pt-containing Lamoreaux catalyst solution were mixed at room temperature under argon. Over 1 h the temperature was raised to 125 °C and maintained for 30 min. Low-boiling materials (b.p. <240 °C/1 mmHg) were distilled off over a 15 cm Vigreux column. The product can be distilled over a 5 cm glass tube. The trisiloxanyl-modified octaethylene glycol derivative ($EO_8$; 4 g, b.p. 249–256 °C/0.75 mmHg) was obtained.

### 2.1.3 Low-energy wafer surfaces

In order to carry out the spreading experiments, low-energy wafer surfaces were synthesized. Thus, a single silicon wafer was cut into four pieces. After ultrasonication in ethanol, methylene chloride and diethyl ether, the pieces were placed in an oxidizing solution consisting of 39 parts of $H_2SO_4$ (conc.), 11 parts $H_2O$ and 2 parts $K_2S_2O_8$ (by weight). The wafer pieces were carefully rinsed with twice-distilled water, dried in an argon stream and placed for 12 h in a vacuum-tight desiccator containing 10 ml hexamethyldisilazane. Finally the trimethylsilyl-modified wafers were rinsed with diethyl ether, ethanol and twice-distilled water.

The surface energy of the four wafer pieces was characterized by contact angle measurements versus water, hexadecane, pentadecane and tetradecane. Test liquid drops were placed on every piece and the contact angles determined goniometrically. The angles (Table 5) represent mean values of at least four measurements. Deviations above $\pm 1°$ for single measurements were not observed. The data for the strictly non-polar alkanes ($\gamma_{lv} = \gamma_{lv}{}^{LW}$) were used to calculate $\gamma_{sv}$ (Ref. 16, Eqn [1]) and $\gamma_{sv}{}^{LW}$ (Ref. 17, Eqn [2]). The practically identical values of $\gamma_{sv}$ and $\gamma_{sv}{}^{LW}$ indicate that this surface is of a non-polar character.[18,19]

$$\cos\theta = \frac{(0.015\gamma_{sv} - 2)\sqrt{\gamma_{sv} \cdot \gamma_{lv}} + \gamma_{lv}}{\gamma_{lv}(0.015\sqrt{\gamma_{sv} \cdot \gamma_{lv}} - 1)} \quad [1]$$

$$1 + \cos\theta = 2\sqrt{\frac{\gamma_{sv}^{LW}}{\gamma_{lv}^{LW}}} \quad [2]$$

## 2.2 Methods

The $^{13}$C-NMR spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ as solvent and internal standard.

Column GC experiments were carried out on a Perkin-Elmer Auto System gas chromatograph, using a 1 m steel column ($\frac{1}{8}$-inch) packed with Chromosorb W-AW-DCMS (80–100 mesh) and modified with 3% SE 30 (temperature program: 50→300 °C, heating rate 10 °C min$^{-1}$, afterwards 20 min at 300 °C, FID).

The GC–MS coupling experiments were carried out on a Hewlett-Packard HP GC 5890/MSD 5970 combination, using a 20 m glass capillary, diameter 0.18 mm, modified with 0.5 μm crosslinked polystyrene DB-5 (temperature program: 1 min at 60 °C; afterwards 60→260 °C, heating rate 20 °C min$^{-1}$; finally 260→280 °C, heating rate 0.5 °C min$^{-1}$, electron impact mass spectra).

Contact angles were measured with an MP 320 goniometer (20-fold magnification, Carl Zeiss Jena).

The spreading experiments were carried out under constant atmospheric conditions (26 °C room temperature, 25 ± 2% relative humidity). Chemicals and equipment had been stored under these conditions for at least 12 h. To guarantee identical wafer surface states (for their preparation, see Section 2.1.3) for all experiments, the following procedure was applied. The wafers were carefully cleaned with water and ethanol, then stored at 50 °C for 5 minutes in a heating chamber. Before new experiments, they were exposed to atmospheric conditions for 5 min. All surfactant solutions were pretreated identically. Immediately before the experiments, water and surfactant were mixed.

**Table 5** Surface energy of the modified silicon wafer calculated from contact angles

| | Liquid | | | |
|---|---|---|---|---|
| | $H_2O$ | $C_{14}H_{30}$ | $C_{15}H_{32}$ | $C_{16}H_{34}$ |
| $\gamma_{lv}$ (mN/m) (20 °C) | 72.6 | 26.6 | 27.3 | 27.6 |
| $\theta$(°) | 91 | 29 | 34 | 38 |
| $\gamma_{sv}$ (mN/m) (Neumann) | | 23.2 | 23.7 | 24.0 |
| $\gamma_{sv}^{LW}$ (mN/m) (Good) | | 23.0 | 23.6 | 23.9 |

These mixtures were handshaken for 2 min and afterwards sonicated for 2 min. For comparative purposes, a few surfactant solutions were investigated before and after ultrasonication. Drops (10 μl) of the surfactant solutions were placed on trimethylsilyl-modified silicon wafers (contact angle vs water 91°; see Section 2.1.3). In order to exclude random errors during the spreading experiments four identically treated wafer pieces were used for each surfactant solution. A standard VHS-C camcorder (25 frames per second) was used to record the spreading drops. The single runs were projected on a conventional TV screen and the drop sizes determined manually. Depending on the spreading velocity, up to 1 frame per second was evaluated. The determination of the starting point (spreading time = 0) was found to be critical. During the drop deposition process, material that spreads well already starts to wet the surface. We had to define a reasonable starting point. Solutions of the derivative bearing three ethylene glycol moieties did not spread and a 10 μl drop covered an equilibrium area of 19.62 $mm^2$. Therefore this area defined the starting point of every spreading experiment.

Dynamic light-scattering experiments were carried out on a Nicomp Submicron Particle Sizer, model 370 (laser light wavelength 633 nm, detection angle 90°, Gaussian distribution of particle sizes, measuring temperature 25 °C). In complete analogy to the pretreatment for spreading experiments, freshly prepared solutions were handshaken and sonicated for 2 min each.

## 3 RESULTS

Figures 1–3 summarize the time dependence of the spreading areas for different surfactant structures and concentrations. It can be seen that both parameters influence the spreading behaviour decisively.

Figure 4 depicts the surprisingly weak influence of the pretreatment on the spreading performance of $EO_6$.

In Fig. 5 the concentration-dependent initial spreading velocities are summarized. The initial velocities increase monotonically with increasing concentration for every surfactant under investigation. $EO_3$ solutions did not spread.

## 4 DISCUSSION

### 4.1 Siloxanyl-modified oligoethylene glycols

Two different strategies were considered to obtain sufficient amounts of defined oligoethylene glycol derivatives of the general structure $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_{3-9}OCH_3$, i.e. isolation of the single species from commercially available product mixtures (Silwet L77) or selective synthesis of these components.

A distillative separation of complex mixtures like Silwet L77 is time-consuming ($\Delta T$ per $CH_2CH_2O$ moiety $\approx$ 20 °C) and restricted to relatively low-boiling species.[20] An alternative chromatographic purification is complicated by the well-known hydrolytic instability of trisiloxane surfactants.[21,22] Polar stationary phases cannot be used and the separation performance of non-polar stationary phases (i.e. RP 18)[15] limited since all species within the mixture bear the dominant trisiloxane moiety.

Therefore we decided to synthesize the individual species selectively. Due to our experience of the Williamson syntheses of the key intermediates, the oligoethylene glycol monoallyl monomethyl ethers $CH_2{=}CHCH_2(OCH_2CH_2)_{3-9}$ $OCH_3$, the following aspects had to be considered. Distillations for allyl derivatives with $n > 5$ had to be carried out as fast as possible since polymerization could take place. The boiling points of starting materials and products preferably differed substantially ($\Delta T > 40$ °C).

In order to avoid an alcoholate-catalysed C1 → C2 double bond shift,[23] we finally incorporated allyloxy moieties via the monochloro derivatives, which could be synthesized under moderate conditions.[15] Additionally, we always dropped the glycolate solution into the halogenide.

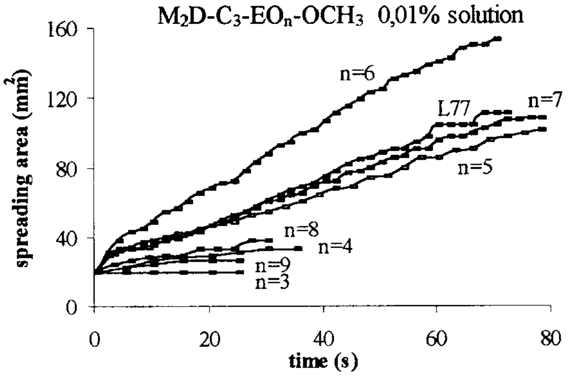


**Figure 1** Time-dependent spreading areas for defined oligoethylene glycol derivatives and Silwet L77; $c = 0.01$ wt%.

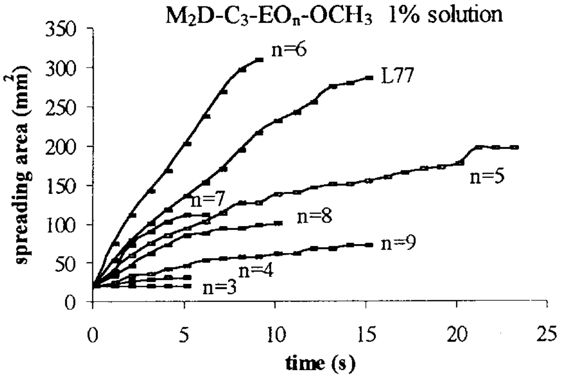


**Figure 3** Time-dependent spreading areas for defined oligoethylene glycol derivatives and Silwet L77; $c = 1$ wt%.

Monomethyl ethers of oligoethylene glycols could be synthesized with high purity. But their ability to form glycolates rapidly decreases with increasing chain length. The only successful possibility of synthesizing these glycolates was to add sodium at elevated temperatures. Attempts to use KOH[14] or $NaOCH_3$[24] failed completely. Due to this rapidly decreasing glycolate formation tendency, we had to synthesize $CH_2{=}CHCH_2(OCH_2CH_2)_4Cl$ as the essential starting material for longer-chained derivatives. Since the boiling points of the corresponding allyl, hydroxy and chloro compounds are similar, we always obtained product mixtures. Fortunately the by-products could be eliminated in the subsequent coupling reactions.

The hydrosilylations proceeded rapidly and with high yields. Nevertheless we distilled all products to eliminate the platinum catalyst and minor impurities. For substances with boiling points above 220 °C/0.7 mmHg, an increasing decomposition tendency was noticed. The GC–MS investigations of the contamination (Table 3) indicated that the oligoethylene glycol chain was cleaved randomly. The silicon-containing impurities were probably formed by elimination of a few terminal ethylene glycol or diethylene glycol species, because their MS patterns contained the typical set of signals for methylsiloxanes and the retention times were very close to those of defined derivatives. On the other hand we found minor amounts of relatively low-boiling and silicon-free materials in the distillates. In these cases the oligoethylene glycol chain was cleaved close to the siloxanyl moiety.

## 4.2 Spreading performance

The spreading behaviour of (oligoethylene glycol)-

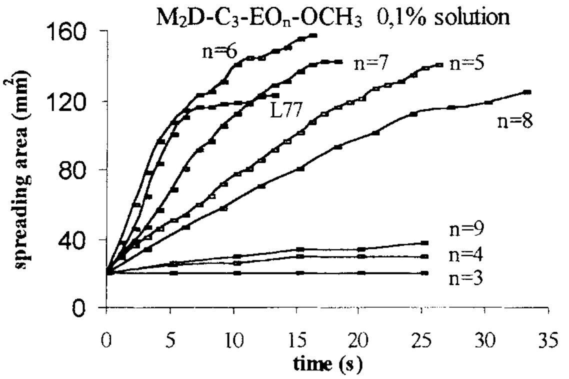


**Figure 2** Time-dependent spreading areas for defined oligoethylene glycol derivatives and Silwet L77; $c = 0.1$ wt%.

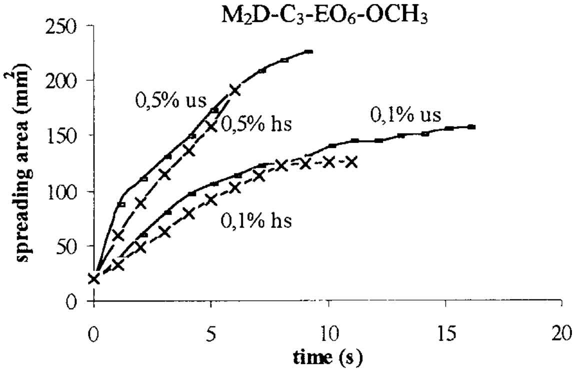


**Figure 4** $EO_6$: dependence of the spreading areas on the surfactant solution pretreatment (us, ultrasonication; hs, handshaken).

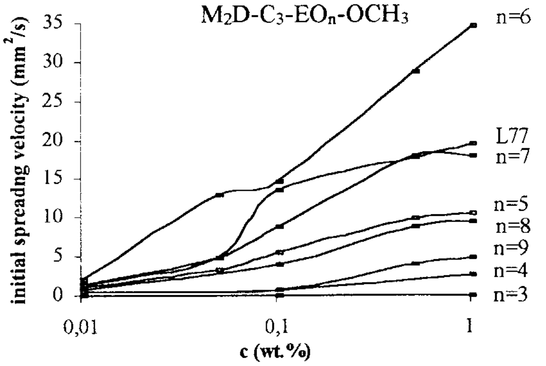


**Figure 5** Concentration-dependent initial spreading velocities (26 °C, 25% relative humidity).

modified trisiloxane surfactants[2,3] and their aqueous solutions has been studied extensively. Here the attention was predominantly focused on the surfactant concentration dependence,[1] the influences of the oligoethylene glycol chain length and hydrophobicity of the solid surface.[4] Since the turbidity of the surfactant solutions was found to be essential for superspreading to occur on low-energy surfaces, the phase behaviour was studied in detail.[8–10] The fact that non-turbid trisiloxane surfactant solutions[4] and solutions of hydrocarbon-based oligoethylene glycol derivatives[5] spread rapidly on moderately hydrophobic solid surfaces proved the existence of a much more general surfactant-enhanced spreading phenomenon.

Nevertheless, the investigation of siloxane surfactants on low-energy surfaces bears one major advantage. The little-understood interplay between short-range polar and long-range non-polar surface energy components of moderately hydrophobic surfaces on the one side and adequate (but possibly varying) surfactant molecule orientations on the other side cannot complicate the situation.[25] The hydrophobic siloxanyl moieties orient towards the hydrophobic solid surface.

It is our view that this advantage can only be used if strictly defined siloxane surfactants are investigated. A comprehensive investigation of the wetting behaviour of strictly defined carbohydrate-modified silicon surfactants clearly demonstrated the influences of the substructures on the energy balances.[18,19,26] Further, it can be shown that amino-functionalized trisiloxane structures possess superspreading properties and even minor changes of the chemical structure (the incorporation of a single methyl group) decisively influence the spreading performance.[18]

The data in Figs 1–3 and 5 support this view. For all concentrations under investigation, a pronounced chain length dependence of the spreading performance was found. For all concentrations under investigation, derivative $EO_6$ showed the best spreading performance (the largest areas occupied and highest initial spreading velocities). $EO_7$ followed, at a substantial distance. $EO_5$ spread slightly better than $EO_8$. $EO_9$ and $EO_4$ were poor spreaders, whereas $EO_3$ did not spread at all. The general trend for large spreading areas accompanied by high initial spreading velocities is very clear.

Apparently this result is in line with the data obtained for commercial mixtures of average compositions $M(D^*EO_4OH)M$, $M(D^*EO_8OH)M$, and $M(D^*EO_{12}OH)M$.[4] The mixture bearing eight ethylene oxide units was found to spread much faster on low-energy surfaces than the more hydrophobic derivative with four ethylene oxide moieties attached to the trisiloxane block and the more hydrophilic derivative with 12 units attached.

Nevertheless a closer inspection of our data raises questions about the meaning of the results obtained for those commercial surfactant mixtures. The data in Figs 1–3 and 5 prove that Silwet L77 spreads significantly faster than all the derivatives under investigation except $EO_6$. If this is true, the high spreading rate of Silwet L77 can be founded exclusively on its $EO_6$ content of roughly 16% (Table 6). Other derivatives alone cannot generate such high velocities. It follows immediately that the basis for a meaningful comparison of mixtures with different molecular weight distributions is a careful analysis of the compositions. Further, these first results emphasize the necessity for the systematic investigation of strictly defined mixtures.

We could not find the known[4] spreading velocity maxima within the concentration range under investigation. The spreading velocities increased monotonical with concentration (Fig. 5). It is interesting to note that this behaviour was found for the pure compounds as well as for Silwet L77. Clearly, Silwet L77 behaves differently on surfaces of varying surface energy and chemistry. Detailed

**Table 6** Composition (wt%) of Silwet L77 according to a GC investigation

| $EO_3$ | $EO_4$ | $EO_5$ | $EO_6$ | $EO_7$ | $EO_8$ | $EO_9$ | $EO_{10}$ | $EO_{11}$ |
|---|---|---|---|---|---|---|---|---|
| 4.0 | 9.6 | 13.1 | 16.2 | 18.1 | 17.2 | 12.1 | 7.0 | 2.7 |

**Table 7** Visible turbidity of surfactant solutions[a]

| Composition (wt.%) | $EO_3$ | $EO_4$ | $EO_5$ | $EO_6$ | $EO_7$ | $EO_8$ | $EO_9$ | Silwet L77 |
|---|---|---|---|---|---|---|---|---|
| 0.01 | t | t | t | nt | nt | nt | nt | nt |
| 0.1 | t | t | t | t | t | nt | nt | t |
| 1 | t | t | t | t | t | t | t | t |

[a] Abbreviations: t, turbid; nt, not turbid.

investigations on the nature of this phenomenon are in progress.

At the present level of understanding the identification of a single component does not provide an answer to the apparently simple question as to the respect in which such a compound decisively differs from closely related but strikingly less effective ones. Since the appearance of turbid solutions is essential for the superspreading effect on low-energy surfaces[1,4] we investigated the chain-length-dependent particle size distribution (Table 3). The average particle size decreases monotonical with increasing oligoethylene glycol chain length. This result reflects the tendency towards increasing water solubility of the long-chain derivatives but does not explain the peculiarity of $EO_6$. The data for handshaken and sonicated solutions support this view (Table 4). Although minor differences were found, the parameter particle size is less important than the chemical structure of the surfactant. Further, since the 0.01 wt% solutions of $EO_6$ and Silwet L77, which are not visibly turbid (Table 7), were spreading much faster than the turbid solutions of $EO_5$ and $EO_4$, the evaluation of this property gives little access to the real nature of the process.

## 5 SUMMARY

Defined oligoethylene glycol modified trisiloxane surfactants can be synthesized from monochloro oligoethylene glycol monoallyl ethers and monomethyl ethers of oligoethylene glycolates and subsequent hydrosilylation of the resulting long-chain monoallyl monomethyl-substituted oligoethylene glycols.

On a trimethylsilylated low-energy surface the solutions of $EO_6$ always occupied the largest spreading areas and showed the highest initial spreading velocities. Silwet L77 and all other defined derivatives followed at a substantial distance.

The spreading velocities increased with concentration. Spreading velocity maxima were not observed.

The average particle size decreased monotonical with increasing oligoethylene glycol chain length and water solubility. Therefore, this parameter cannot explain the peculiarity of $EO_6$.

For handshaken and sonicated solutions of $EO_6$, minor differences were found. However, the parameter pretreatment is less important than the chemical structure of the surfactant.

Despite an intensive investigation of the turbidity (the existence of a one- or two-phase state), a meaningful correlation between phase behaviour and spreading performance does not appear to exist. This statement is founded on two experimental results. On one hand, temperature-dependent spreading experiments did not provide any clear-cut trend.[4] On the other hand, a correlation between phase behaviour and spreading performance of aqueous solutions of ethoxylated alcohols ($C_iE_j$) on moderately hydrophobic surfaces could not be established. Whether this argument holds or has to be understood as part of a broader rule will be discussed in separate papers.

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## REFERENCES

1. S. Zhu, W. G. Miller, L. E. Scriven and H. T. Davis, *Colloids Surf.* **90**, 63 (1994).
2. F. Tiberg and A. M. Cazabat, *Europhys. Lett.* **25**, 205 (1994).
3. F. Tiberg and A. M. Cazabat, *Langmuir* **10**, 2301 (1994).
4. T. Stoebe, Z. Lin, R. M. Hill, M. D. Ward and H. T. Davis, *Langmuir* **12**, 337 (1996).
5. T. Stoebe, Z. Lin, R. M. Hill, M. D. Ward and H. T. Davis, *Langmuir* **13**, 7270 (1997).
6. T. Stoebe, Z. Lin, R. M. Hill, M. D. Ward and H. T. Davis, *Langmuir*, **13**, 7276 (1997).
7. T. Stoebe, Z. Lin, R. M. Hill, M. D. Ward and H. T. Davis, *Langmuir*, **13**, 7282 (1997).

8. M. He, R. M. Hill, Z. Lin, L. E. Scriven and H. T. Davis, *J. Phys. Chem.* **97**, 8820 (1993).
9. Z. Lin, R. M. Hill, H. T. Davis, L. E. Scriven and Y. Talmon, *Langmuir* **10**, 1008 (1994).
10. M. He, Z. Lin, L. E. Scriven and H. T. Davis, *J. Phys. Chem.* **98**, 6148 (1994).
11. T. Svitova, H. Hoffmann and R. M. Hill, *Langmuir* **12**, 1712 (1996).
12. H. Haidara, M. K. Chaudhury and M. J. Owen, *J. Phys. Chem.* **99**, 8681 (1995).
13. R. Wagner, Y. Wu, L. Richter, S. Siegel, J. Weißmüller and J. Reiners, *Appl. Organometal Chem.* **12**, 843 (1998).
14. S. Schüring and W. Ziegenbein, *Tenside* **4**, 161 (1967).
15. R. Fordyce, E. L. Lovell and H. Hibbert, *J. Am. Chem. Soc.* **61**, 1905 (1939).
16. O. Driediger, A. W. Neumann and P.-J. Sell, *Kolloid Z. Z. Polym.* **201**, 101 (1965).
17. C. J. van Oss, M. J. Chaudhury and R. J. Good, *Chem. Rev.* **88**, 927 (1988).
18. R. Wagner, L. Richter, J. Weißmüller, J. Reiners, K.-D. Klein, D. Schaefer and S. Stadtmüller, *Appl. Organometal. Chem.* **11**, 617 (1997).
19. R. Wagner, L. Richter, Y. Wu, J. Weißmüller, J. Reiners, E. Hengge, A. Kleewein and K. Hassler, *Appl. Organometal. Chem.* **11**, 645 (1997).
20. G. Czichocki, H. Brämer and I. Ohme, *Z. Chem.* **20**, 90 (1980).
21. M. Knoche, H. Tamura and M. J. Bukovac, *J. Agric. Food Chem.* **39**, 202 (1991).
22. K.-D. Klein, W. Knott and G. Koerner, Silicone surfactants—development of hydrolytically stable wetting agents. In: *Organosilicon Chemistry II*, Auner, N. and Weis, J. (eds), VCH, Weinheim, 1996, pp. 613–618.
23. Houben/Weyl, *Methoden der Organischen Chemie*, Vol. 6/3, G. Thieme Verlag, Stuttgart, 1965, p.183.
24. W. Gerhardt, *Monatsber. Dtsch. Akad. Wiss. Berlin* **9**, 922 (1967).
25. E. Ruckenstein, *J. Colloid Interface Sci.* **179**, 136 (1996).
26. R. Wagner, L. Richter, Y. Wu, B. Weiland, J. Weißmüller, J. Reiners, E. Hengge and A. Kleewein, *Appl. Organometal. Chem.*, **12**, 47 (1998).