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Silicon-modified Surfactants and Wetting: V. The Spreading Behaviour of Trimethylsilane Surfactants on Energetically Different Solid Surfaces†

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The spreading behaviour of defined trimethylsilane-based surfactants of general formula $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)_nOCH_3$, $n = 2–6$, on five different solid surfaces at 21 °C has been investigated. Compounds bearing short diethylene and triethylene glycol hydrophiles do not spread. For the longer-chained tetraethylene to hexaethylene glycol derivatives, the ability to spread depends on the surface energy. Rapid spreading is restricted to the slightly polar surface of 40 mN m^{-1} surface energy. Lower or higher surface energies considerably reduce the spreading rates. The phase behaviour of the solutions substantially influences the spreading process. The dispersed systems of the tetraethylene glycol derivative spread constantly over long time intervals. The dispersions of the pentaethylene glycol analogue are very close to the temperature for a transition into the one-phase state. A retardation of the spreading process occurs after a few seconds. Micellar solutions of the hexaethylene glycol derivative either spread very slowly or stop spreading after a few seconds. The largest spreading areas and highest initial spreading rates were found for the 0.1 wt% solutions. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: surfactants; trimethylsilanes; wetting; spreading behaviour

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1 INTRODUCTION

Aqueous solutions of some commercially available trisiloxane surfactants rapidly wet hydrophobic as well as moderately hydrophilic surfaces ($\cos\theta_{water}$ 0 to 0.9). For Silwet L77 (in which a polydisperse triethylene to dodecaethylene glycol hydrophile is attached to the trisiloxane moiety via a short trimethylene spacer) a maximum is found for $\cos\theta_{water} = 0.4$.[1,2] The spreading rate of such a so-called 'superspreader' solution significantly exceeds that expected for a process purely controlled by liquid diffusion.[3–5] It is assumed that fast adsorption of surfactant molecules onto the substrate produces a surface tension gradient which generates a rapid flow (Marangoni flow) of surfactants directed towards the drop edge.[2,6,7]

The importance of the turbidity of trisiloxane surfactant solutions for spreading on low-energy surfaces has been stressed repeatedly.[2,8] However, it could be shown that certain additives generate non-turbid solutions and simultaneously increase the spreading rate.[9] Recent papers focus on the general ability of certain trisiloxane-based surfactants to form vesicles as an essential prerequisite for superspreading, or on the formation of a separate phase of accumulated surfactant molecules at the solid–liquid interface.[10,11] These partially contrary findings are due to the complex composition of commercially available superspreaders which prevents a comprehensive understanding of the phenomenon.[12]

A recent investigation of strictly defined trisiloxane-based species has definitely shown that superspreading depends decisively on the phase state and the surface energy/surface chemistry, R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, in press. Furthermore, the spreading temperature and the composition of

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Table 1 Composition [percentage of $(CH_3)_3Si\ (CH_2)_6\ (OCH_2\ CH_2)\ m\ OH$] of K4237 according to a GC analysis

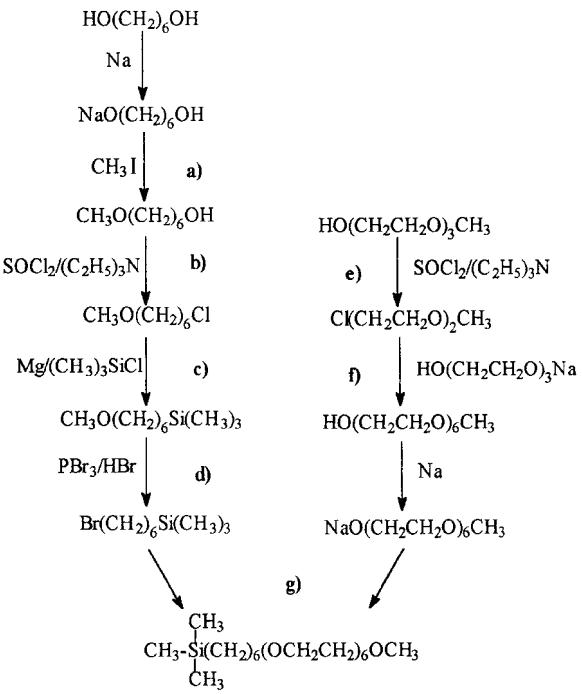
m	1	2	3	4	5	6	7	8
	5.2	14.7	19.1	21.8	17.5	13.3	7.2	1.2

binary or ternary surfactant mixtures play important roles. (Ref. 13; see also R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, in press; R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal. Chem.*, AOC 13, 201 (1999); R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin, T. Rexin and L. Perepelittchenko, *Appl. Organometal. Chem.*, AOC 885; R. Wagner, Y. Wu and H. v. Berlepsch, *Monatsh. Chem.*, 130, 237 (1999).

However, the question for the necessity of the trisiloxane moiety in strictly defined superspreaders has not been answered. The major disadvantage of trisiloxane-based structures is their hydrolytic instability.[14,15] Therefore alternative structures have been investigated. Oligoethylene glycol derivatives of fatty alcohols (C_iE_j) spread rapidly on high-energy surfaces.[8] Branched polysilane and carbosilane structures have also been considered.[16–18]

Due to the better accessibility and surprisingly low solution surface tensions,[19] hydrolytically stable polydisperse trimethylsilane superspreaders have been developed (e.g. Goldschmidt K4237).[20–22]

It is the purpose of this study to describe the synthesis of defined trimethylsilane-based oligoethylene glycol derivatives and to investigate the dependences of their spreading areas and initial spreading rates on the surface energy and surface polarity. In addition, the properties of these materials are compared with those of corresponding trisiloxane surfactants.



Scheme 1 Reaction sequence yielding the trimethylsilyl-substituted hexaethylene glycol derivative.

2 MATERIALS AND METHODS

2.1 Materials

Silwet L77 and K4237 were supplied from Union Carbide and Goldschmidt AG, respectively. K4237 is a polydisperse surfactant of general formula $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)_mOH$, $m = 1–8$. The composition is given in Table 1.

Defined trimethylsilyl derivatives of the general type $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)nOCH_3$, $n = 2–6$ ($SiEO_2$ to $SiEO_6$), have been synthesized in a complex reaction sequence from the corresponding oligoethylene glycol monomethyl ethers (Scheme 1).

Key intermediates for the synthesis of these defined derivatives are 1-bromo-6-trimethylsiyl-hexane and the corresponding oligoethylene glycol monomethyl ethers. The latter have been synthesized from monochloro oligoethylene glycol monomethyl ethers and oligoethylene glycols via subsequent halogenations (e) and Williamson etherifications (f).[23,24] 1-Bromo-6-(trimethylsilyl)hexane has been synthesized from 1,6-hexanediol. The multistep reaction sequence includes an etherification (a) and halogenations (b and d) as well as a Grignard type reaction (c). The apparently straightforward hydrosilylation of hex-5-en-1-ol with trimethylsilane[21] was not used since the handling of large amounts of the gaseous silane was found to be difficult under laboratory conditions.[19]

Table 2 Chain lengths and boiling points of oligoethylene glycol intermediates and the trimethylsilyl derivatives $SiEO_2$ to $SiEO_6$

$Cl(CH_2CH_2O)_mCH_3$ (B.p., °C/mmHg)	$HO(CH_2CH_2O)_nCH_3$ (B.p., °C/mmHg)	$(CH_3)_3Si(CH_2)_6O(CH_2CH_2O)_nCH_3$ (B.p., °C/mmHg)	purity (%)	Contamination (%)	
				Si	Without Si
	2 (194/760*)	$SiEO_2$ (110–113/0.35)	>>99		
	3 (122/10*)	$SiEO_3$ (162–166/0.8)	>>99		
2 (164–174/760)	4 (112–118/0.3)	$SiEO_4$ (188–190/0.7)	>>99		
2	5 (148–153/0.5)	$SiEO_5$ (193–195/0.2)	>>99		
3 (112–114/16)	6 (167–169/0.6)	$SiEO_6$ (206–211/0.3)	98	2 ($SiEO_5$)	

* commercially available (Aldrich)

Table 2 summarizes structures and boiling points of key oligoethylene glycol intermediates and the trimethylsilyl derivatives $SiEO_2$ –$SiEO_6$.

According to GC–MS experiments, $SiEO_6$ contains minor amounts of $SiEO_5$. Retention time and fragmentation pattern (signals at $m/z = 59$ [$CH_3OCH_2CH_2$], 103 [$CH_3OCH2CH_2OCH_2CH_2$] and 73 [$(CH_3)_3Si$]) are identical to those of the pure compound $SiEO_5$.

Table 3 contains the structure-confirming ^{13}C-NMR signals for derivative $SiEO_2$.

2.1.1 Synthesis of $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)_6OCH_3$ ($SiEO_6$)

Procedure (a)

Hexane-1,6-diol 1500 g; 12.69 mol) was placed under argon in a four-necked bottle equipped with refluxing condenser, thermometer and stirrer. The temperature was raised to 70 °C. Over 1.5 h 114 g (4.96 mol) of sodium were added and the temperature was simulataneously raised to 130 °C. Afterwards the reaction mixture was cooled to 60 °C. Over 2 h 780 g (5.4 mol) CH_3I was dropped in. The temperature was then kept at 70 °C for an additional 2 h. Four vacuum distillations over a 30 cm Vigreux column yielded 150 g of a crude product (b.p. 106–110 °C/20 mmHg). The synthesis described above of the monomethyl ether was repeated three times. The crude products were UNCLEAR TEXT distilled twice over a 50 cm packed column. Colourless 1-hydroxy-6-methoxyhexane 377 g; (b.p. 100–103 °C/14 mmHg, GC purity 99.5%) was obtained.

Procedure (b)

1-Hydroxy-6-methoxyhexane (377 g; 2.86 mol) was placed in a three-necked bottle equipped with refluxing condenser, dropping funnel, magnetic stirrer and argon inlet. After cooling to 10 °C, 357 g (3 mol) of thionyl chloride was added over 1h. The temperature was raised to 60 °C at the end of the addition. Three vacuum distillations over a 50 cm packed column yielded 205.5 g of the colourless 1-chloro-6-methoxyhexane (b.p. 70–71 °C/14 mmHg, GC purity 98%).

Procedure (c)

Magnesium (35 g; 1.44 mol) and I_2 (10 mg) were placed in a three-necked bottle equipped with refluxing condenser, dropping funnel, magnetic stirrer and argon inlet. Absolute THF (20 ml) and 20.5 g (0.14 mol) 1-chloro-6-methoxyhexane were added. The temperature was raised to 50 °C and the reaction started. The mixture was diluted with 100 ml THF. A mixture of 185 g (1.23 mol) 1-

Table 3 ^{13}C-NMR shifts of selected substructures of derivative $SiEO_2$

Substructure	$(CH_3)_3Si$	$SiCH_2$	$SiCH_2CH_2$	OCH_3
Shift (ppm)	−1.94	16.34	23.56	58.64

chloro-6-methoxyhexane and 500 ml THF was added over 1 h. Due to the exothermic reaction the temperature rapidly rose to 65 °C. After 50% addition the system was further heated to maintain the temperature. The mixture was cooled to 55 °C and 172 g (1.58 mol) trimethylchlorosilane was added over 1 h. To complete the reaction the temperature was raised to 70 °C for 3 h. After cooling to room temperature, $MgCl_2$ and traces of magnesium were filtered off, THF was removed at atmospheric pressure and the residue was subjected to two vacuum distillations over a 25 cm packed column. 1-Methoxy-6-trimethylsilylhexane (181 g, b.p. 84–86 °C/16 mmHg, GC purity 96%) was obtained as a colourless liquid.

Procedure (d)
1-Methoxy-6-trimethylsilylhexane (181 g; 0.96 mol) was placed in a four-necked bottle equipped with a dropping funnel, stirrer, thermometer and a refluxing condenser with attached water separator. After cooling to 0 °C 302 g (1.12 mol) phosphorus tribromide was added over 10 min. The temperature was raised to 80 °C and 50 ml hydrobromic acid (48 wt%) was added to the solution over 1.5 h. After cooling to 0 °C, 80 ml of water was injected. The organic layer was separated and dried over Na_2SO_4. Vacuum distillation over a 25 cm packed column yielded 205 g of the colourless 1-bromo-6-trimethylsilylhexane (b.p. 104 °C/14 mmHg, GC purity 98%).

Procedure (e)
Triethylene glycol monomethyl ether (739 g; 4.5 mol) and 505 g (5 mol) triethylamine were placed in a four-necked bottle equipped with refluxing condenser, dropping funnel, stirrer and thermometer. After cooling to 10 °C 596 g (5 mol) thionyl chloride was added over 2 h. At the end of the addition the temperature was raised to 70 °C. The black reaction mixture was cooled to room temperature and liquefied by addition of diethyl ether. After filtration the collected diethyl ether extracts were combined, the solvent was distilled off and the residue was subjected to two vacuum distillations. The colourless monochloro triethylene glycol monomethyl ether (666 g; b.p. 112–114 °C/17 mmHg, GC purity 99.5%) was obtained.

Procedure (f)
Triethylene glycol (870 g; 5.8 mol) was placed in a three-necked bottle equipped with refluxing condenser, dropping funnel, magnetic stirrer and argon inlet. The temperature was raised to 70 °C and 38 g (1.65 mol) sodium pieces were added to the liquid. Due to the exothermic reaction the temperature immediately started to rise. By controlled sodium addition it was maintained at 120 °C for 1 h. Monochloro triethylene glycol monomethyl ether (298.5 g; 1.64 mol) was dropped into the hot glycolate over 40 min. Sodium chloride immediately started to precipitate. To complete the reaction the temperature was raised to 170 °C for 1 h. After cooling to room temperature the mixture was diluted with diethyl ether and filtered. The solvent was removed and the crude product twice was distilled over a 25 cm packed column. The distillations yielded 250 g hexaethylene glycol monomethyl ether (b.p. 167–169 °C/0.6 mmHg, GC purity 95%).

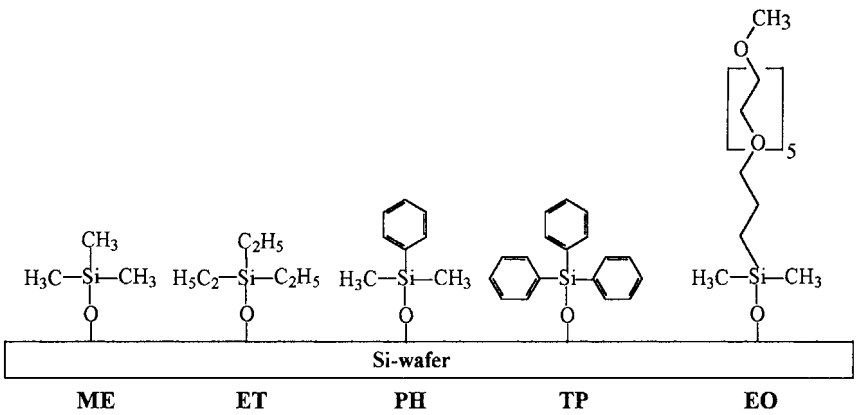
Procedure (g)
Hexaethylene glycol monomethyl ether (115.4 g; 0.39 mol) was placed in a three-necked bottle equipped with refluxing condenser, dropping funnel, magnetic stirrer and argon inlet. The temperature was raised to 160 °C and 3 g (0.13 mol) sodium was dissolved in the liquid over 1 h. Due to the exothermic reaction and additional heating the temperature increased to 200 °C. The mixture was cooled to 100 °C and 30 g (0.13 mol) 1-bromo-6-trimethylsilylhexane was dropped into the hot glycolate over 15 min. Sodium bromide immediately started to precipitate. To complete the reaction the temperature was raised to 170 °C for 1 h. After cooling to room temperature the mixture was filtered and the crude product distilled three times over a 10 cm Vigreux column. The distillations yielded 9 g of the trimethylsilyl-substituted hexaethylene glycol monomethyl ether derivative $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)_6OCH_3$ (b.p. 206–211 °C/0.3 mmHg, GC purity 98%).

2.1.2. Spreading experiments

For the spreading experiments five chemically and energetically different silicon wafer surfaces were prepared. The chemical structures and solid surface energy data are summarized in Scheme 2 and Table 4. The surface modification methods and the characterization of the surface energies have been outlined (R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, in press).

2.2 Methods

^{13}C-NMR spectra were recorded on a Varian XL



Scheme 2 Surface structures of the modified silicon wafers.

300 spectrometer using $CDCl_3$ as solvent and internal standard.

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

The GC–MS coupling experiments were carried out on a Hewlett-Packard HP GC 5890/MSD 5970 combination. 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, then 60 °C→ 260 °C, heating rate 20 °Cmin^{-1}, finally 260 °C→ 280 °C, heating rate 0.5 °Cmin^{-1}, electron impact mass spectra) was used.

Dynamic light scattering experiments were carried out on a Zetasizer 3000 (Malvern; laser light wavelength 633 nm, detection angle 90°, Gaussian distribution of particle sizes, measuring temperature 21 °C). In complete analogy to the pretreatment for spreading experiments, freshly prepared solutions were handshaken and each was sonicated for 2 min. Typically, 0.01 wt% solutions have been investigated. In order to reach a sufficient signal intensity a 1 wt% solution of $SiEO_6$ had to be used.

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

The general procedure for the spreading experiments has been described elsewhere (Ref. 13 and R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, **13**, 621 (1999); R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal. Chem.*, **13**, 201 (1999); R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin, T. Rexin and L. Perepelittchenko, *Appl. Organometal. Chem.*, AOC 885).

The spreading experiments on the surfaces of the different silicon wafers were carried out in a laboratory maintained at 21 ± 0.5 °C and 49 ± 2% relative humidity. Chemicals and equipment had

Table 4 Modified silicon wafer surfaces: solid surface tensions (γ_{sv}), Lifshitz–van der Waals (γ_{sv}^{LW}), donor–acceptor ($\gamma_{sv}^{+/-}$) contributions and water contact angles

	ME	ET	PH	TP	EO
γ_{sv} (mNm^{-1}) (Neumann[a])	23	30	41	42	47
γ_{sv}^{LW} (mNm^{-1}) (Good[b])	23	30	39	41	46
$\gamma_{sv}^{+/-}$ (mNm^{-1}) (Owens[c])	0	0	1	3	4
$\gamma_{sv}^{tot} = \gamma_{sv}^{LW} + \gamma_{sv}^{+/-}$ (mNm^{-1})	23	30	40	44	50
water contact angle (°)	93	90	79	59	46

[a] Ref. 25.
[b] Ref. 26.
[c] Ref. 27.

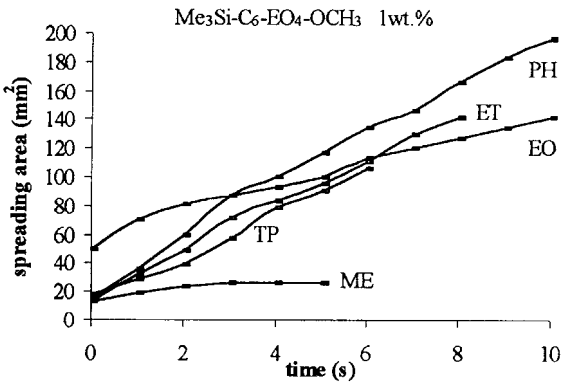


Figure 1 Time-dependent spreading areas for the derivative $SiEO_4$; c = 1 wt%.

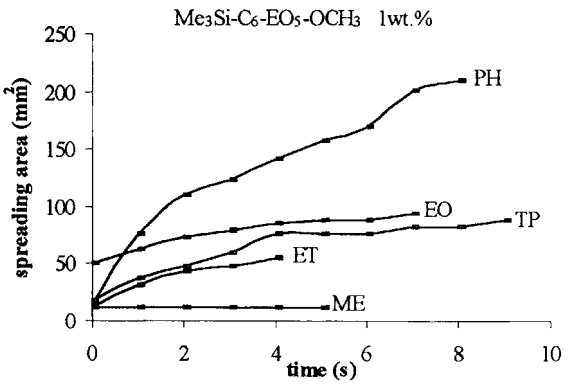


Figure 3 Time-dependent spreading areas for the derivative $SiEO_5$; c = 1 wt%.

been stored under these conditions for at least 12 h. The wafers were carefully cleaned with twice-distilled water, ethanol and finally twice-distilled water. Prior to every new experiment they were exposed to atmospheric conditions for 5 min. The mixtures were handshaken for 2 min and afterwards ultrasonicated for 2 min in a water bath. A microsyringe was used to deposit 10 μl drops of the surfactant solutions on the modified silicon wafers.

Each spreading experiment was repeated twice with identically pretreated wafers. A standard VHS-C camcorder (25 frames per second) was used to record the spreading drops. The single runs were visualized on a conventional TV screen and the drop sizes were determined manually. Depending on the spreading rate, up to 1 frame per second was evaluated. The setting of the starting points (spreading time = 0) was critical. Drops (10 μl) of a 1 wt% solution of the trisiloxane-based derivative $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_3OCH_3$ did not spread and covered equilibrium areas of 12.5 mm^2 (ME), 12.5 mm^2 (ET), 14.9 mm^2 (PH), 17.5 mm^2 (TP) and 50.2 mm^2 (EO), respectively. These areas defined the starting points of the spreading experiments. For a given time the mean spreading areas have been calculated from the single-run data. Typically, the deviation of single-run areas from the mean values is less than 10%. Initial spreading rates have been calculated from the slopes of the area vs time curves. In order to avoid impacts from the drop deposition process, the minimum time interval for the calculations was 3 s.

The samples for the phase investigations were prepared by mixing the surfactants with twice-distilled water in glass test-tubes. After mixing the solutions were subjected to a heating and cooling cycle for solubilizing and homogenizing the mixtures. The phase transition temperatures were determined after equilibration by visual inspection of the solutions in a thermostated water bath between crossed polarizers. The temperature at which the mixtures change from transparent to turbid can be determined this way with an accuracy of $\pm$ 0.1 °C. Birefringence indicates the presence of anisotropic liquid-crystalline phases. Flow birefringence was observed by stirring.

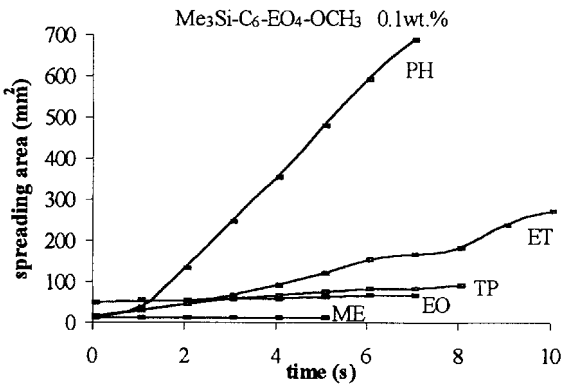


Figure 2 Time-dependent spreading areas for the derivative $SiEO_4$; c = 0.1 wt%.

3 RESULTS

Figures 1–8 describe the time dependence of the spreading areas for 1 wt% and 0.1 wt% solutions of

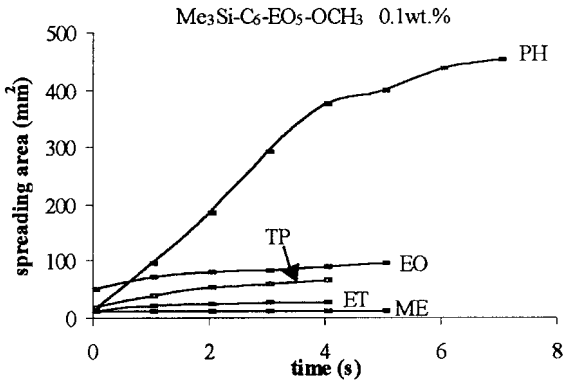


Figure 4 Time-dependent spreading areas for the derivative $SiEO_5$; $c = 0.1$ wt%.

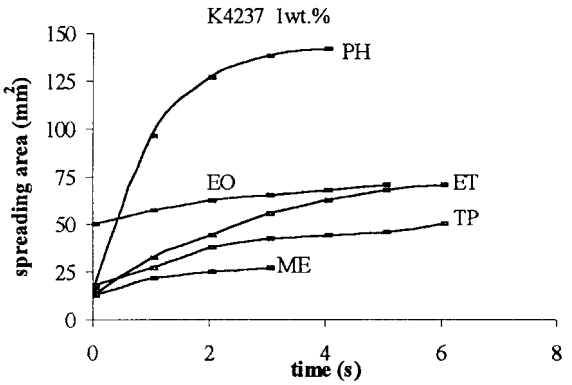


Figure 7 Time-dependent spreading areas for K4237; $c = 1$ wt%.

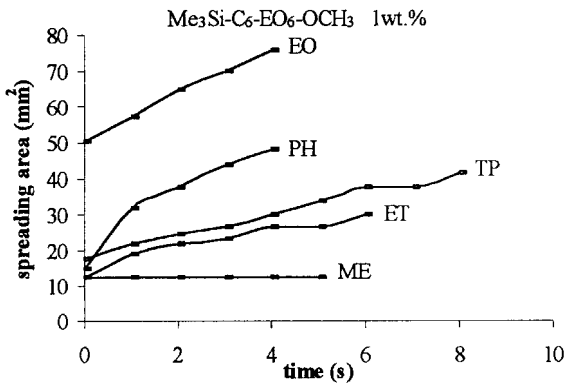


Figure 5 Time-dependent spreading areas for the derivative $SiEO_6$; $c = 1$ wt%.

the single compounds $SiEO_4$, $SiEO_5$ and $SiEO_6$ as well as the polydisperse surfactant K4237.

The largest spreading areas are found on the PH surface for the 0.1 wt% solutions. The concentrated 1 wt% systems cover smaller areas. The 0.1 wt% $SiEO_6$ and the 1 wt% K4237 solutions stop spreading after a few seconds.

Figures 9–12 depict the concentration and surface energy dependence of the initial spreading rates for the derivatives $SiEO_4$ to $SiEO_6$ and K4237. The single compounds as well as the polydisperse system reach the spreading rate maximum on the PH surface. The 0.1 wt% solution of $SiEO_4$ is the only one with a noticeable spreading rate on the ET surface. Substantially reduced initial spreading rates were found on the extremely low-energy ME as well as on the high-energy TP and EO surfaces.

For comparative purposes the corresponding

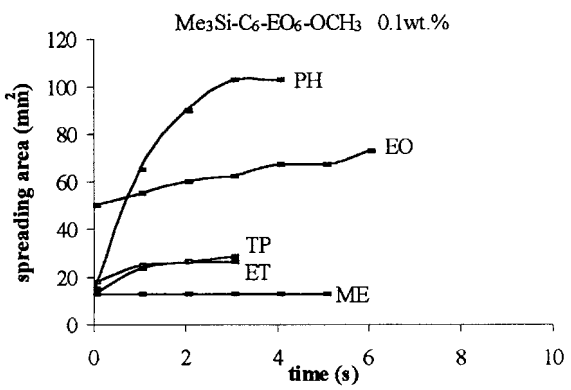


Figure 6 Time-dependent spreading areas for the derivative $SiEO_6$; $c = 0.1$ wt%.

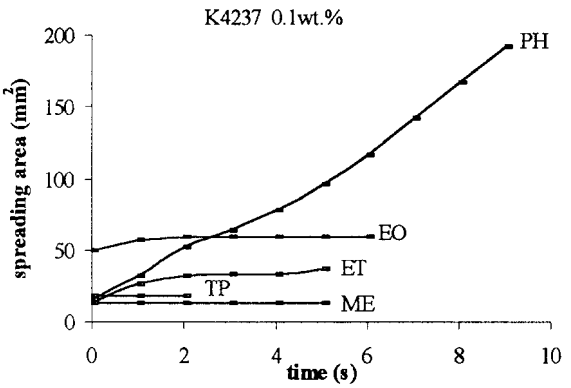


Figure 8 Time-dependent spreading areas for K4237; $c = 0.1$ wt%.

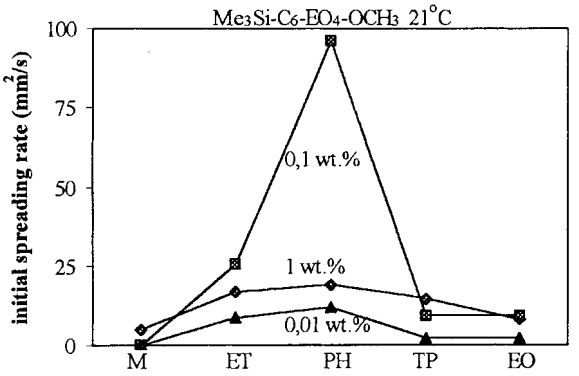


Figure 9 $SiEO_4$: concentration and surface energy dependence of the initial spreading rates.

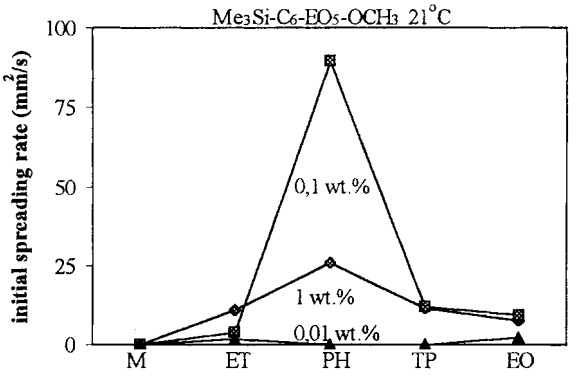


Figure 10 $SiEO_5$: concentration and surface energy dependence of the initial spreading rates.

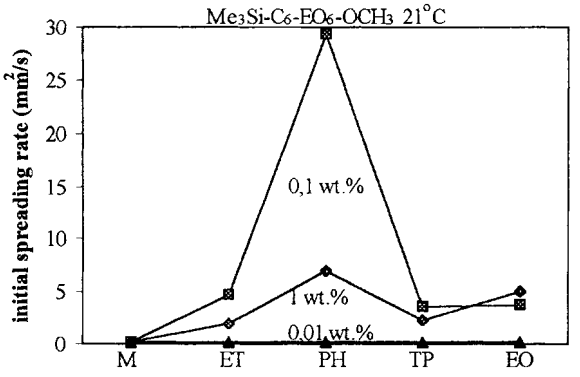


Figure 11 $SiEO_6$: concentration and surface energy dependence of the initial spreading rates.

spreading rates of the trisiloxane-based materials $[(CH_3)_3SiO]_2$ $CH_3Si(CH_2)_3$ $(OCH_2CH_2)_6$ OCH_3 (EO_6, Fig. 13) and Silwet L77 (Fig. 14) have been

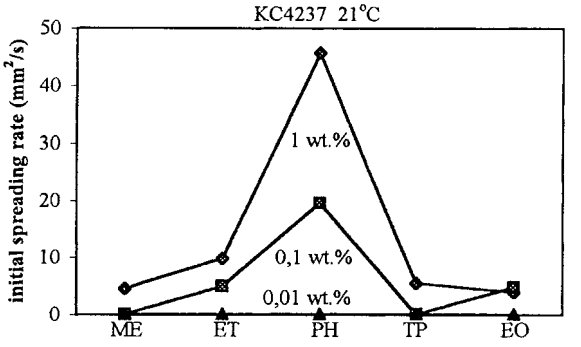


Figure 12 K4237: concentration and surface energy dependence of the initial spreading rates.

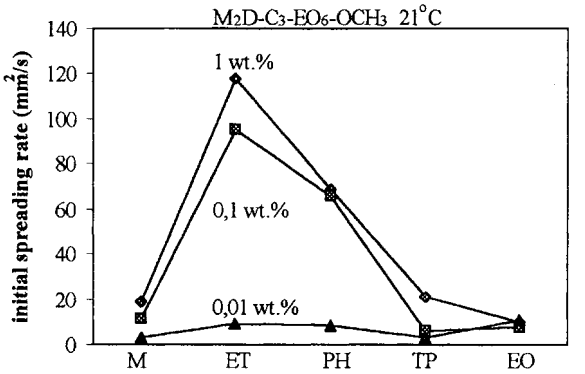


Figure 13 Defined trisiloxane surfactant EO_6: concentration and surface energy dependence of the initial spreading rates (data taken from R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, in press.).

included R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, in press. Both surfactants spread rapidly on the ET and PH surfaces.

Figure 15 summarizes the phase transition temperatures of 1 wt% and 5 wt% solutions of the single compounds $SiEO_3$ to $SiEO_6$ and K4237. The solutions of $SiEO_4$ are more or less turbid at low temperatures and show birefringence. On increasing the temperature the solutions become transparent and show the typical texture of a lamellar phase between crossed polarizers. We assume by analogy with related hydrocarbon-[28] and siloxane-based compounds[29–31] that the mixtures are dilute dispersions of bilayer aggregates (L_α phase). Upon increasing the temperature the solutions become flow-birefringent (L_3 phase). further temperature increase yields cloudy but isotropic solutions which show complete phase separation after 12 h. This

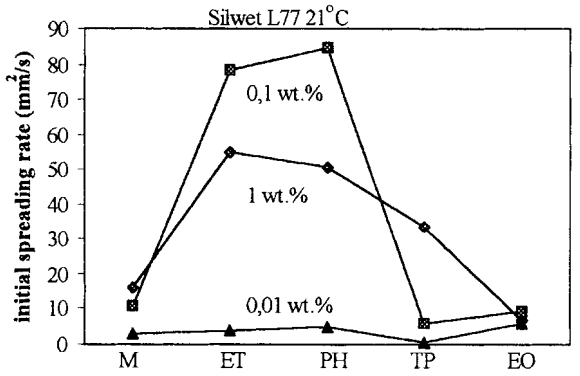


Figure 14 Silwet L77: concentration and surface energy dependence of the initial spreading rates (data taken from R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem*., in press.).

two-phase state is designated 2Φ and the liquid–liquid insolubility boundary is specified as the cloud point T_c.

The solutions of $SiEO_5$ and $SiEO_6$ are transparent at low temperatures and do not show birefringence. They become cloudy and isotropic at T_c. Complete phase separation is reached after 24 h. The existence of a micellar solution at low temperatures is suggested. Lamellar or sponge phases have not been observed.

The 1 wt% solution of the polydisperse K4237 is turbid at low temperatures. It possesses a complex phase behaviour. Within 7 days at 24 °C it separates into an upper flow-birefringent (L_α) and a bottom flow-birefringent (L_3) phase. Upon increasing the temperature it becomes cloudy and isotropic at 28.6 °C.

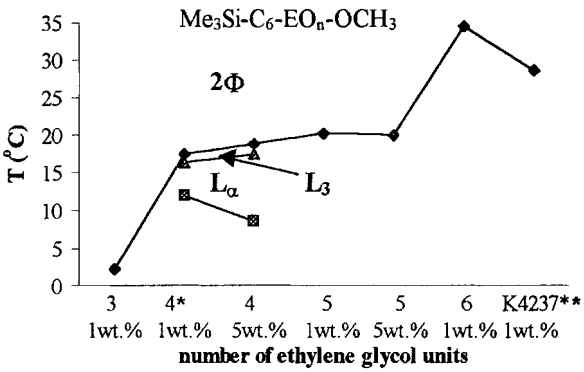


Figure 15 Phase transition temperatures as a function of the oligoethylene glycol chain length and concentration. *Two-phase L_3 region: upper surfactant rich L_3 layer, bottom water layer. **After 7 days at 24 °C two phases: upper L_α layer, bottom L_3 layer.

4 DISCUSSION

It was demonstrated recently R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem*., in press. that the spreading behaviour of solutions of defined trisiloxane surfactants depends on the surface energy. The 1 wt% solutions of the relatively short-chain pentaethylene glycol (EO_5) and hexaethylene glycol (EO_6) derivatives rapidly spread on the nonpolar ET surface. On the slightly polar PH surface, dilute 0.1 wt% solutions of the heptaethylene glycol (EO_7) and octaethylene glycol (EO_8) derivatives spread faster. Furthermore, spreading behaviour and phase behaviour are closely related. This change in the spreading pattern coincides with that of the phase behaviour. At 21 °C spreading temperature, solutions of EO_5 and EO_6 represent dispersed two-phase systems (2Φ) whereas EO_7 and EO_8 form vesicular/lamellar ones.

Defined trimethylsilane-based surfactants behave differently. Solutions of the short-chain derivatives $SiEO_2$ and $SiEO_3$ did not spread on the surfaces under investigation. Due to their short oligoethylene glycol chains, macroscopic phase separation occurred rapidly.

For the compounds $SiEO_4$, $SiEO_5$ and $SiEO_6$ (Figs 9–11) a uniform pattern of the initial spreading rates has been found. Rapid spreading is restricted on the slightly polar PH surface and diluted 0.1 wt% solutions. The more concentrated or diluted systems spread more slowly. Furthermore, the initial spreading rates are substantially reduced on the nonpolar, low-energy surfaces ME and ET as well as on the polar, high-energy surfaces TP and EO. Clearly these defined trimethylsilane-based materials do not possess the inherent ability of trisiloxane surfactants to spread rapidly on nonpolar, low-energy surfaces like ET (Fig. 13). However, for the derivative bearing the shortest oligoethylene glycol chain, $SiEO_4$, the highest initial spreading rate on the ET surface was found (Fig. 9). Diverging from the typical trisiloxane behaviour (Fig. 13) the 0.1 wt% solution spreads faster than the 1 wt% one. Nevertheless, if rapid and complete phase separation can be avoided, short-chain derivatives open up the possibility of wetting materials of nonpolar, low-energy, character. R.

Table 5 Particle sizes of solutions of $SiEO_4$, $SiEO_5$ and $SiEO_6$

Derivative	$SiEO_4$ (0.01 wt%)	$SiEO_5$ (0.01 wt%)	$SiEO_6$ (1 wt%)
Particle size (intensity mean, nm)	240	221	11

Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, *Appl. Organometal. Chem.*, in press.

The polydisperse surfactant K4237 (Fig. 12) spreads significantly more slowly than $SiEO_4$ and $SiEO_5$. It is reasonable to assume[2] that the head-group difference (i.e. —OH for K4237 and —OCH_3 for $SiEO_4$) is not responsible for the substantially reduced initial spreading rates. Intriguingly, in this particular case the 1 wt% solution spreads faster than the dilute 0.1 wt% one. A comparison with the polydisperse Silwet L77 (Fig. 14) is of practical interest. It immediately discloses that without performance-enhancing measures K4237 cannot compete with the trisiloxane surfactant. The dilute 0.1 wt% solution of the latter spreads faster and on a broader range of acceptable surfaces.

Experiments with defined trisiloxane surfactants have proved that dispersed (2Φ) as well as lamellar/vesicular phases are able to generate rapid spreading. R. Wagner, Y. Wu, H. v. Berlepsch and L. Perepelittchenko, Appl. Organometal. Chem., in press. Probably due to water evaporation at the spreading front and the subsequent formation of viscous lamellar phases, the 1 wt% systems of the latter phase type abruptly stop spreading after a few seconds. Dispersed systems spread for much longer.

According to Figs 1 and 2, $SiEO_4$ solutions can spread over long time intervals on the PH surface. At a spreading temperature of 21 °C they represent dispersed two-phase systems (Fig. 15). $SiEO_5$ solutions behave slightly differently. Although the spreading process does not stop, kinks in the area vs. time curves (Figs. 3 and 4) are clearly visible. In this particular case T_c (20.3 °C, Fig. 15) is only slightly below the spreading temperature and therefore the driving force for a complete phase separation is small. Nevertheless, due to dynamic light-scattering data (Table 5) the solutions of both $SiEO_4$ and $SiEO_5$ consist of large particles typical for dispersed systems. It is important to note that for $SiEO_5$ at 21 °C a lamellar phase region appears at a concentration as high as 55 wt%. R. Strey, R. Wagner, Langmuir, in press. This evident difficulty of forming the highly concentrated lamellar phase seems to be responsible for the transitional character of the area vs. time curves.

$SiEO_6$ solutions consist of substantially smaller particles (Table 4). Spreading of these micellar systems is retarded to such an extent that the shape of the 1 wt% curve cannot be evaluated reliably (Fig. 5). Surprisingly, the 0.1 wt% solution stops spreading after a few seconds (Fig. 6).

K4237 behaves like a long-chain trisiloxane surfactant in a lamellar/vesicular state (Figs 7 and 8). The concentrated 1 wt% solution stops spreading abruptly after a few seconds, whereas the 0.1 wt% one continues to wet the solid surface.

4.1 Conclusion

The spreading behaviour of solutions of single trimethylsilane-based surfactants on solid materials depends decisively on the surface energy. Rapid spreading is restricted to slightly polar surfaces (PH) of medium surface energy (40 mN m^{-1}).

The spreading behaviour on the PH surface and phase behaviour are related. The dispersed (2Φ) systems of $SiEO_4$ constantly spread over long time intervals. For the solutions of $SiEO_5$, close to T_c, a retardation of the spreading process after a few seconds is clearly visible. The solutions of $SiEO_6$ either spread very slowly (1 wt%) or stop spreading after a few seconds (0.1 wt%).

The polydisperse K4237 spreads more slowly and over smaller areas than the most active single compounds $SiEO_4$ and $SiEO_5$ and the polydisperse trisiloxane surfactant Silwet L77.

Diverging from the behaviour of defined trisiloxane surfactants, the single trimethylsilane-based materials always spread over larger areas and faster at the 0.1 wt% concentration.

The data for defined trisiloxane-and trimethylsilane-based single compounds indicate that short-chain species tend to spread faster on low-energy surfaces. Therefore, an examination of defined mixtures consisting of short-and long-chain derivatives could help to improve the understanding of the role of single components in complex mixtures.

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