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Silicon-modified Surfactants and Wetting: II. Temperature-dependent Spreading Behaviour of Oligoethylene Glycol Derivatives of Heptamethyltrisiloxane

R. Wagner,[1]* Y. Wu,[1] G. Czichocki,[1] H. v. Berlepsch,[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

The temperature-dependent spreading performance of defined trisiloxane surfactants of the general formula $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_{3-9}OCH_3$ and Silwet L77 on a trimethylsilylated silicon-wafer surface has been investigated. At 6 °C the tetraethylene glycol derivative showed the highest initial spreading rate. At 40 °C the octaethylene glycol derivative was the fastest spreader. It is shown that spreading behaviour and phase behaviour are closely related. The highest initial spreading rates were found for solutions in the two-phase state (2Φ) closely above the liquid–liquid insolubility boundary. Copyright © 1999 John Wiley & Sons, Ltd.

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1 INTRODUCTION

Aqueous solutions of certain commercially available trisiloxane surfactants (i.e. Silwet L77; a polydisperse triethylene to dodecaethylene glycol hydrophile is attached to the trisiloxane moiety via a short trimethylene spacer) rapidly wet low-energy surfaces (water contact angle >90 °).[1] The spreading rate of such a so-called 'superspreader' solution significantly exceeds that expected for a purely liquid diffusion-controlled process.[2–4]

The analysis of spreading data obtained for the systems silicon-surfactant solution/low-energy solid surface[5] and silicon-surfactant solution/liquid hydrocarbon interface[6,7] led to the assumption that this rapid spreading is a Marangoni-flow-driven process. It is suggested that fast adsorption of surfactant molecules onto the substrate produces a surface tension gradient which generates a flow directed towards the drop edge.

However, this assumed spreading mechanism does not conclusively explain apparently contradictory experimental results. On the one hand the importance of turbidity of the solutions for spreading on low-energy surfaces has been stressed.[5,8] For pure surfactants of the oligoethylene glycol type a turbid two-phase state can be reached by temperature adjustment.[9–12] On the other hand experiments demonstrated that the spreading behaviour of the polydisperse Silwet L77 is nearly independent of the temperature and the phase state of the solution.[5] Furthermore, aqueous solutions of oligoethylene-glycol-modified hydrocarbons (C_iE_j) rapidly wet moderately hydrophobic solid surfaces.[5,8] The spreading rates of these defined surfactants do not correlate with a certain microstructure of the solutions.[8] Instead, a pronounced spreading rate dependence on the oligoethylene glycol chain length was found.

Recently we showed[13] that aqueous solutions of certain amino-modified trisiloxane structures rapidly spread on polypropylene. Minor changes of the amino moiety structure caused considerable differences in the spreading area. This finding clearly suggests that a better understanding of super-

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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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spreading on low-energy surfaces necessitates the investigation of sufficiently pure substances. In a companion paper† we describe the synthesis of single components of Silwet L77 bearing three to nine oligoethylene glycol units attached to the trisiloxane block. We showed that under defined experimental conditions (hydrophobic surface, contact angle $\theta = 91$ ° vs water, 26 °C, 25% relative humidity) the spreading of the derivative bearing six ethylene glycol moieties is superior to that of all other ones. Nevertheless the identification of a single compound does not answer the question of which property decisively distinguishes this molecule from chemically closely related ones.

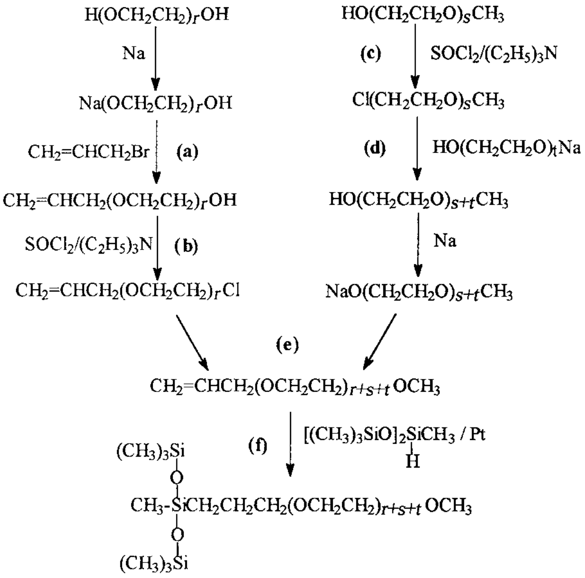
Therefore the purpose of this study was to investigate the temperature dependence of the spreading rate as well as the corresponding phase behaviour of defined trisiloxane derivatives bearing three to nine ethylene glycol moieties.

2 MATERIALS AND METHODS

2.1 Materials

The synthesis of defined 1,1,1,3,5,5,5-heptamethyltrisiloxanyl (MD*M) derivatives of the general structure $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_{3-9}OCH_3$ has been outlined in detail in the companion paper. A complex reaction sequence including halogenations (b, c), Williamson-type etherifications (a, d, e) and hydrosilylations (f) was applied (Scheme 1).

Table 1 summarizes the colours, purities and product compositions of the siloxanyl-modified oligoethylene glycols.[14]



Scheme 1 Reaction sequence yielding defined oligoethylene glycol derivatives of 1,1,1,3,5,5,5-heptamethyltrisiloxane.

Table 1 Colours, purities and contamination contents of the siloxanyl-modified oligoethylene glycols

	Colour	Purity (% GC)	Contamination (%)	
			Si	Without Si
EO3	Colourless	≫99		
EO4	Colourless	≫99		
EO5	Colourless	99		1
EO6	Pale yellow	97.5	1 (EO5 type)	1.5
EO7	Pale yellow	96	1.5 (EO6 type)	2.5
EO8	Yellow	95	1.5 (EO6 type)	3.5
EO9	Pale brown (Pt)	90	10 (EO7 + EO8 type)	

For the spreading experiments low-energy wafer surfaces were prepared. 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 conc. $H_2SO_4/H_2O/K_2S_2O_8$ (39:11:2 by wt). The wafer pieces were carefully rinsed with bidistilled 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 bidistilled water.

Before the experiments the four wafer pieces were energetically 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 2) represent the mean values of at least four measurements. Deviations larger than ±1 ° for single

Table 2 Surface energy of the modified silicon wafer calculated from contact angles

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

measurements were not observed. The data for the strictly non-polar alkanes ($\gamma_{\mathrm{lv}} = \gamma_{\mathrm{lv}}^{\mathrm{LW}}$) were used to calculate γ_{sv} (Ref. 14. Eqn 1, in which the surface energies are dimensionless) and $\gamma_{\mathrm{sv}}^{\mathrm{LW}}$ (Ref. 15; Eqn 2). The good agreement between the γ_{sv} and $\gamma_{\mathrm{sv}}^{\mathrm{LW}}$ values indicates the non-polar character of the surface.[13,16]

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

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

where
θ = contact angle
γ_{sv} = solid surface tension
γ_{lv} = liquid surface tension
$\gamma_{\mathrm{sv}}^{\mathrm{LW}}$ = Lifshitz–van der Waals portion of the solid surface tension
$\gamma_{\mathrm{lv}}^{\mathrm{LW}}$ = Lifshitz–van der Waals portion of the liquid surface tension.

2.2 Methods

The spreading behaviour of aqueous surfactant solutions has been investigated under two different atmospheric conditions.

Low-temperature experiments were carried out in a laboratory kept at 6 ± 0.5 °C and 45 ± 2% relative humidity. Before the experiments chemicals and equipment were stored under these conditions for at least 12 h. To guarantee identical wafer surface properties they were pre-treated as follows. The hydrophobic wafers were carefully cleaned with bidistilled water, ethanol and finally bidistilled water. Prior to every new experiment they were exposed to atmospheric conditions for 5 min. All surfactant solutions were prepared in the same way. Immediately before the experiments water and surfactant were mixed. The mixtures were shaken manually for 2 min and afterwards ultrasonicated for 2 min in a water bath at 6 °C. A microsyringe was used to deposit 10 μl of the surfactant solutions on the trimethylsilyl-modified silicon wafers (contact angle vs water 91°).

The high-temperature experiments were carried out in the same laboratory but on a heating plate kept at 40 ± 2 °C (3.2 g H_2O/m^3 air, 6% relative humidity on the plate surface). The wafers were cleaned as described above. Before the experiments they were placed on the heating plate for at least 5 min in order to reach the desired temperature and a constant humidity level. The temperature of freshly prepared surfactant solutions was adjusted separately in a water bath at 40 °C. Afterwards they were shaken and ultrasonicated (2 min). In order to avoid changes in the temperature of the solutions, we always deposited the drops on the wafer surface within a few seconds.

To minimize the error, every single spreading experiment was repeated four times with identically pre-treated wafers. A standard VHS-C camcorder (25 frames/s) 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/s was evaluated. As outlined in the companion paper[14] the determination of the starting point (spreading time = 0) was critical. Since during the drop deposition process the best spreaders had already started to wet the surface, we had to define this starting point. The 10 μl drops of the 0.01 wt% solution of the triethylene glycol derivative EO3 did not spread, and covered at equilibrium an area of 22.33 mm^2. This area defined the starting point of every spreading experiment. For a given time the mean spreading areas were calculated as the average from the single-run data. Typically, the deviation of single-run results from the mean values is less than 10%.

The dynamic viscosities of 0.01 wt%, 0.1 wt% and 1 wt% solutions of the short-chain compound EO5 and the long-chain derivative EO8 were determined at 6, 26 and 40 °C (thermostated Ubbelohde viscometer, capillary constant 0.01; Schott Mainz). Any significant influence of the surfactant type or the concentration on the viscosity has not been observed. Typically, we found viscosities of 1.52 mPa s (6 °C), 0.87 mPa s (26 °C) and 0.63 mPa s (40 °C), respectively.

The samples for the phase investigations were prepared by mixing the surfactant with Milli-Q deionized water in glass test-tubes. The phase transition temperatures were determined as a function of the oligoethylene glycol chain length. 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 changed from transparent to turbid can easily be determined in this way with an accuracy of ±1 °C. Birefringence indicates the presence of anisotropic liquid-crystalline phases. Stirring allowed us to observe flow birefringence.

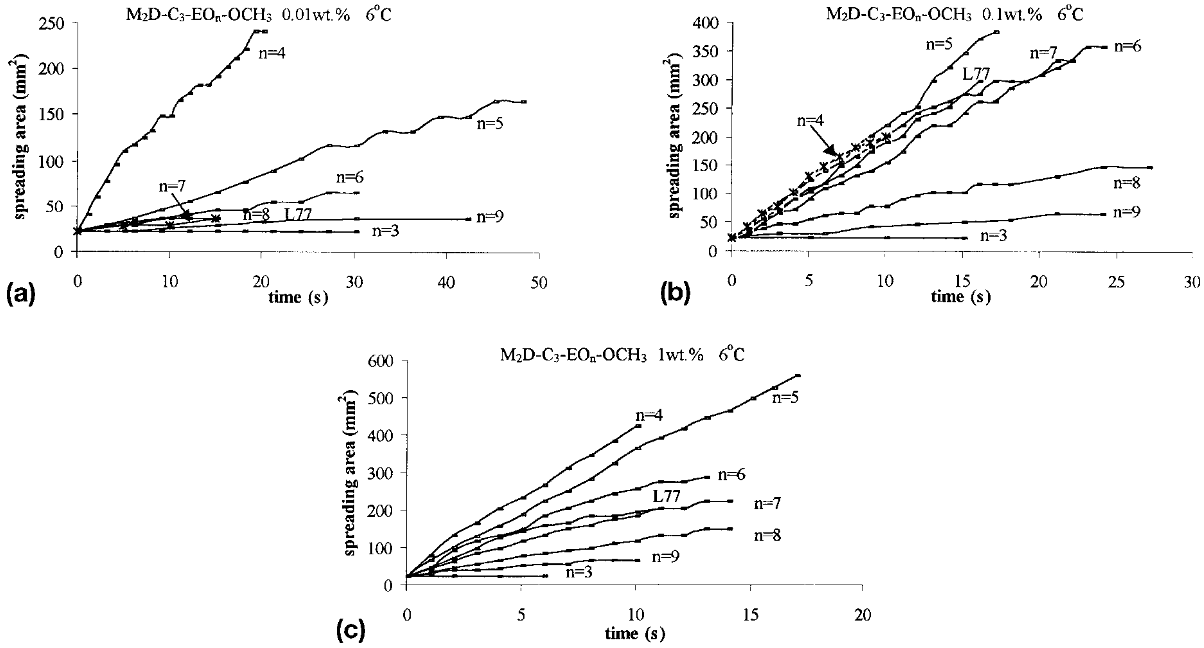


Figure 1 Time-dependent spreading areas for defined oligoethylene glycol derivatives and Silwet L77 at 6 °C and 45% relative humidity: (a) $c = 0.01$ wt%; *, curves for $n = 7$, $n = 8$ and L77 are superposed; (b) $c = 0.1$ wt%; *, $n = 4$; (c) $c = 1$ wt%.

3 RESULTS

Figure 1(a–c) summarizes the concentration - dependent spreading areas at 6 °C and 45% relative humidity. It can be seen that both the surfactant structure and the concentration considerably influence the spreading behaviour: the higher the concentration, the faster the spreading process. The corresponding initial spreading rates are shown in Fig. 2. For every concentration under investigation, EO4 was the fastest spreader.

Figures 3 and 4 depict the corresponding data for 40 °C and 45% relative humidity. Under these conditions EO8 is the fastest spreader. At elevated temperatures the steepest increase of the spreading rate with concentration was observed. On the other hand, the ability to spread was restricted to only a few surfactant homologues.

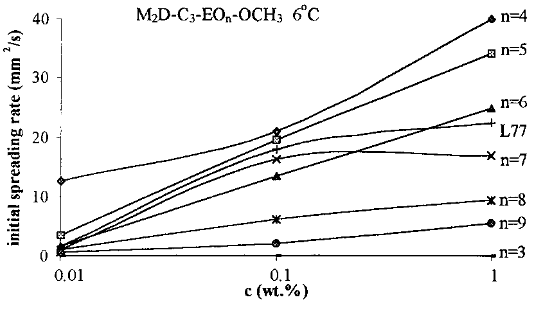


Figure 2 Concentration-dependent initial spreading rates at 6 °C and 45% relative humidity.

It is important to compare the low- and high-temperature data with those for an intermediate temperature. Figure 5 shows the initial spreading rates as a function of the concentration for 26 °C and 25% relative humidity.

Figure 6 summarizes the initial spreading rates as a function of the number of ethylene glycol units for different temperatures and concentrations. The curves exhibit distinct maxima. These maxima shift to longer ethylene glycol chains upon increasing the temperature.

The results of the phase investigations are summarized in Fig. 7. We only prepared surfactant solutions of two concentrations (1 and 5 wt%, respectively), and determined the phase transition temperatures. The general pattern of the phase behaviour of the defined derivatives in this low concentration range is very similar and agrees qualitatively with that for the commercially available polydisperse trisiloxane superspreaders.[10,11] All surfactant solutions are more or less turbid at low temperatures and showed birefringence. When the temperature is increased, the solutions under investigation became increasingly transparent and

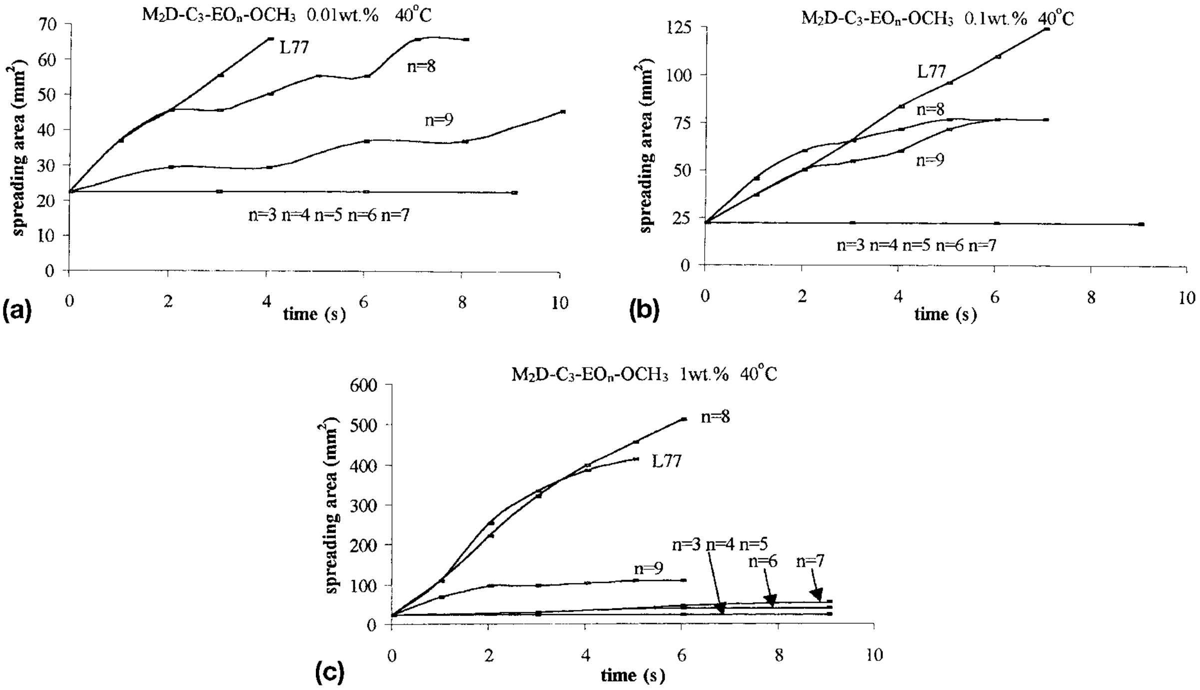


Figure 3 Time-dependent spreading areas for defined oligoethylene glycol derivatives and Silwet L77 at 40 °C and 45% relative humidity: (a) $c = 0.01$ wt%; (b) $c = 0.1$ wt%; (c) = 1 wt%.

showed the typical texture of a lamellar phase between crossed polarizers. Additionally, some solutions showed iridescent colours. Without having investigated the structure of the solutions we assume by analogy with related hydrocarbon[12] and siloxane-based compounds[10,11] that the mixtures are dilute dispersions of bilayer aggregates (L_α phase). When the temperature is increased, a transition occurs from the lamellar L_α phase into a flow birefringent phase which we identified as a sponge phase (L_3 phase). This isotropic lamellar phase has already been found for polydisperse trisiloxane surfactants.[10] The phase exists only in a very narrow temperature range of $\Delta T \sim 1$ °C at 5 wt%. It could not be reliably identified at 1 wt%. Above the L_3 phase the samples again become cloudy but isotropic. This liquid–liquid insolubility boundary may be specified by a cloud point (cf. the discussion in Ref. 10). This state is designated as 2Φ in Fig. 7. Macroscopic phase separation is a slow process for the solutions under investigation and occurs after about two days. The phase

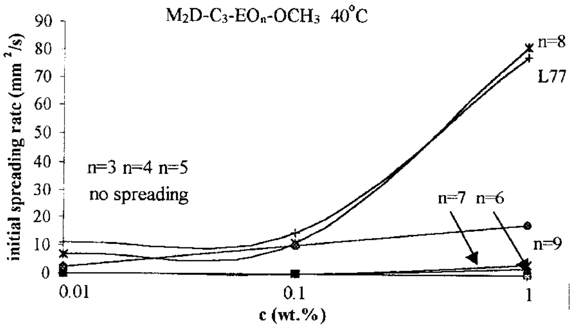


Figure 4 Concentration-dependent initial spreading rates at 40 °C and 45% relative humidity.

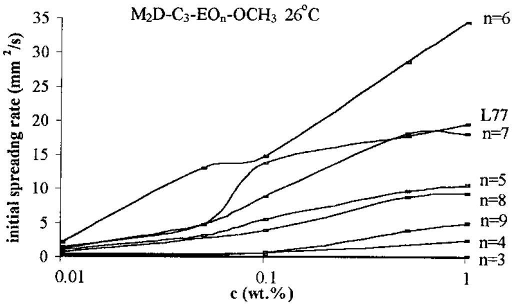


Figure 5 Concentration-dependent initial spreading rates at 26 °C and 25% relative humidity.

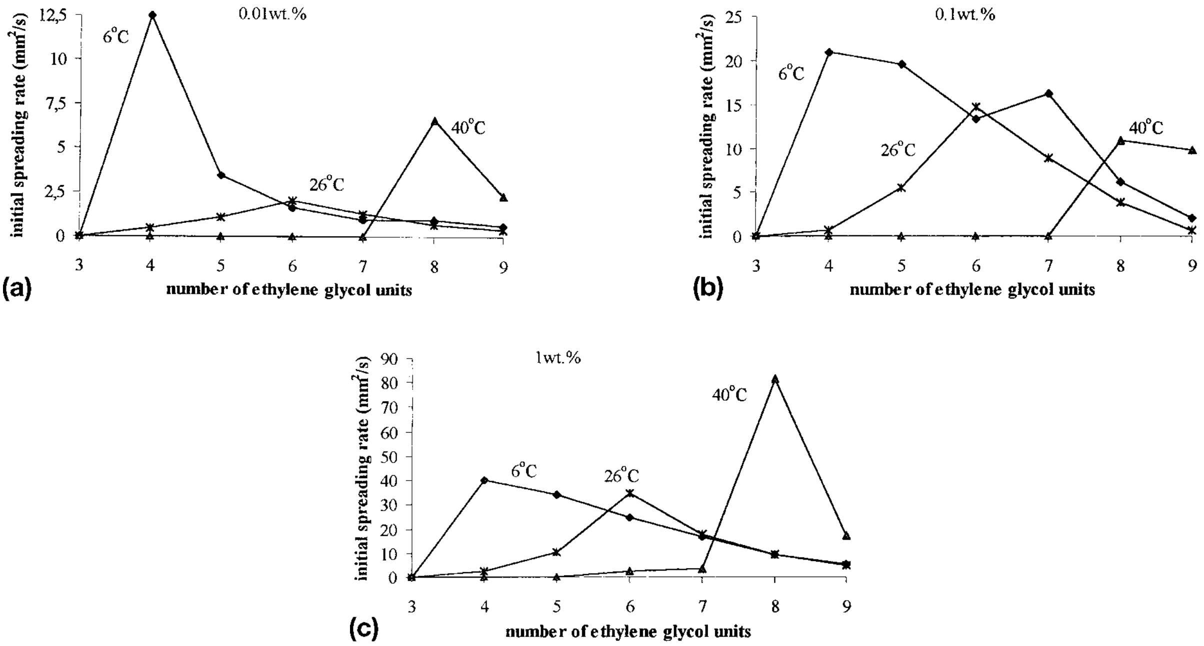


Figure 6 Temperature-dependent initial spreading rates for surfactant solutions at ((a) $c = 0.01$ wt%; (b) $c = 0.1$ wt%; (c) $c = 1$ wt%).

transition temperatures weakly depend on concentration.

The lower phase transition temperatures of EO9 compared with those of EO8 might be due to the short-chain impurities of the EO7 and EO8 type (Table 1). However, despite the presence of considerable amounts of short-chain species, Silwet L77 possesses higher phase transition temperatures. Since a systematic investigation of the phase behaviour of binary, ternary or even more complex mixtures of very long-chain oligoethylene glycol derivatives has not been published, the question of the nature of this transition temperature decrease from EO8 to EO9 remains unsolved.

4 DISCUSSION

The temperature-dependent spreading experiments were carried out in order to answer the question of whether rapid spreading on low-energy, non-polar surfaces is linked to the presence of a single trisiloxane-based surfactant structure or if there is a more general principle. Our own experiments at 26 °C had clearly shown that the derivative EO6 is the superior spreader (Fig. 5). On the other hand, the spreading rates of the complex mixture Silwet L77 have been known to be nearly temperature-independent.[5]

At 6 °C the derivative EO4 shows the best

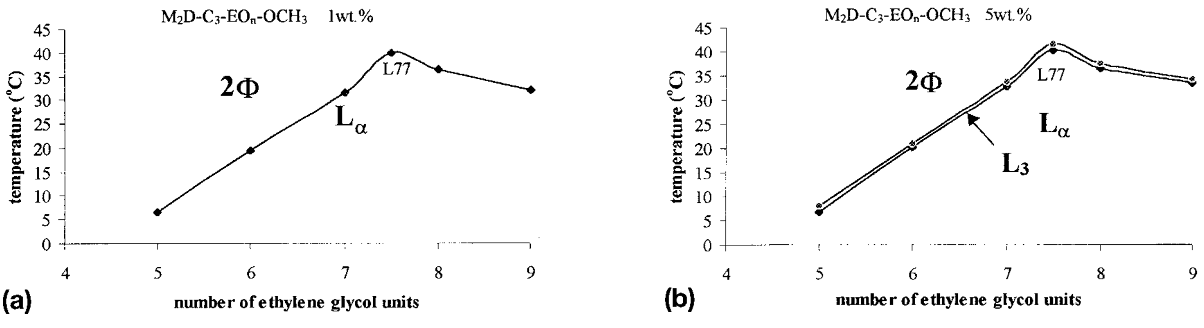


Figure 7 Phase transition temperatures as a function of the oligoethylene glycol chain length: (a) $c = 1$ wt%; (b) $c = 5$ wt%.

spreading performance. At every concentration under investigation (Figs 1 and 2) it possesses the highest initial spreading rates. The derivatives EO5–EO9 follow in the order of increasing oligoethylene glycol chain length. Intriguingly, derivative EO3 did not spread at all.

This result deviates fundamentally from that obtained at 26 °C (Fig 5), where a pronounced spreading maximum for the derivative EO6 was found. A comparison of the 6 °C and 26 °C measurements immediately leads to the important conclusion that a single trisiloxane-based oligoethylene glycol superspreader does not exist.

In order to obtain more information about the spreading mechanism, experiments have been carried out, at 40 °C showing that the derivative EO8 is the best spreader at elevated temperatures (Figs 3 and 4). The derivatives EO9 and EO7 (1 wt%) follow at a substantial distance. The compounds EO3, EO4, EO5, EO6 and EO7 ($c < 1$ wt%) did not spread at all. This behaviour markedly deviates from that at 6 °C, where all derivatives (with the exception of EO3) were found to spread. Moreover, we observed the highest initial spreading rate for the 1 wt% solution of EO8.

Similarly to our previous experiments discribed in the companion paper at 26 °C (Fig. 5), we found a monotonic concentration dependence of the spreading rate at 40 °C. The higher the concentration, the faster the spreading process. It is noteworthy that the steepest increase of the spreading rate is observed at 40 °C (Figs 4 and 6). Obviously a narrow window exists for an optimized spreading process.

It is known that the phase behaviour of surfactants bearing oligoethylene glycol moieties exhibits a strong temperature dependence (Refs 10–12; H.V. Berlepsch and R. Wagner, unpublished work) Hence, the question arises of whether the pronounced temperature dependence of the spreading rates for a given surfactant and the phase behaviour are related. Figure 7 depicts the phase transition temperatures as a function of the oligoethylene glycol chain length. The transition temperatures increase nearly linearly up to derivative EO8. It is obvious that spreading is considerably enhanced after crossing over into the two-phase state above the characteristic temperature T_c. The time needed for macroscopic phase separation is much longer than the duration of the spreading experiment and the solutions are metastable and turbid. For the derivative EO4, T_c is below zero. Thus the system is located in the 2Φ state at 6 °C. A corresponding favourable situation exists for EO6 at 26 °C and EO8 at 40 °C. In both cases the relation $T > T_c$ holds.

It is also important to note that the spreading rate is maximum closely above T_c and decreases on further temperature increase (Fig. 6). A relationship between turbidity and spreading behaviour has been known for a long time. Moreover, the presence of a certain degree of turbidity has been accepted as a precondition for rapid spreading.[5,8] However, it has to be noted that solutions below T_c in the L_α phase are also cloudy and able to spread. Their spreading rates decrease with increasing distance to the phase transition $L_\alpha \rightarrow (L_3) \rightarrow 2\ \Phi$. Nevertheless, at 6 °C even the long-chain derivatives EO8 and EO9 spread considerably.

The experimental results presented here definitely show that the existence of droplets of dispersed surfactants in the two-phase state just above T_c lead to the highest spreading rates. Demixing is a kinetically controlled process. When the temperature and the distance to the phase transition temperature are increased, the droplets are expected to grow. Obviously the lower spreading rates of EO5 compared with those of EO6 at 26 °C (Fig. 5) result from larger droplet sizes in the EO5 dispersions. The enhancement of demixing at high temperatures is visible from Fig. 4, summarizing the spreading results at 40 °C. Only the derivative EO8 with $T_c = 36$ °C shows a high spreading rate at 1 wt%.

The time dependence of demixing should also reduce the spreading performance of dispersions in the 2Φ state stored at a fixed temperature. Although detailed investigations have not been carried out, first explorative experiments have confirmed this suggestion. However because of the known equilibration of the trisiloxane moiety[9,17] (H. V. Berlepsch and R. Wagner, unpublished work) in aqueous systems, an interfering effect of changes in the chemical structure cannot be excluded.

The complex mixture Silwet L77 does not show a pronounced temperature dependence of the spreading rate.[5] It spreads rapidly at 6 °C (Fig. 2) as well as 26 °C (Fig. 5) and is an excellent spreader at 40 °C (Fig. 4). From the high phase transition temperature (Fig. 7a) one would exclusively expect an excellent high-temperature spreading performance. Obviously complex surfactant mixtures behave fundamentally differently. Spreading experiments with mixtures of defined compounds could help to explain this behaviour and are in progress.

Summarizing, we conclude that a single superspreading surfactant molecule does not exist. The ability to spread on low-energy surfaces is the property of an appropriate hydrophobe (i.e. trisiloxane unit). The hydrophilic moiety adjusts the phase state. Spreading behaviour and phase state are closely related. Rapid spreading results from the existence of dispersed surfactant droplets above T_c. Due to the thermodynamic metastability of these dispersions, superspreading strongly depends on the sample pretreatment. Surfactant systems in the thermodynamically stable L_α phase also spread. However, the spreading rates are considerably reduced. For systems above and below T_c the relative distance to the phase transition temperature has a strong influence on the spreading rates. The closer a given system is located relative to T_c the faster the solution spreads.

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