APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 621–630 (1999)

Silicon-modified Surfactants and Wetting: III. The Spreading Behaviour of Equimolar Mixtures of Nonionic Trisiloxane Surfactants on a Low-energy Solid Surface†

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The spreading behaviour of binary and ternary equimolar mixtures of siloxane surfactants of general formula $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_nOCH_3$, $n = 3$–9, has been investigated. The mixtures show a pronounced temperature dependence on the initial spreading rate. Mixtures imitating the average oligoethylene glycol chain length $n = 5$ are the fastest spreaders at 15 °C. At 23 °C and 40 °C these mixtures spread fastest sucking $n = 6$ and $n = 8$, respectively. For a given average chain length an increasing length difference between the components of the binary mixtures reduces the initial spreading rate. Nevertheless, substantial differences between the phase transition temperature T_c from the lamellar phase (L_α) into the two-phase state (2Φ) and the actual spreading temperature are tolerated. A clear relation between phase transition temperature T_c and initial spreading rate does not exist. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: siloxane; surfactants; mixtures; spreading behaviour

Received 9 September 1998; accepted 3 February 1999

1 INTRODUCTION

Aqueous solutions of some commercially available trisiloxane surfactants (e.g. Silwet L77, in which 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 process controlled purely by liquid diffusion.[2–4]

It is suggested that the fast adsorption of surfactant molecules to the substrate produces a surface tension gradient which generates a rapid surfactant molecule flow (Marangoni flow) directed towards the drop edge.[5–7]

However, apparently contradictory experimental results cannot be explained. The importance of the turbidity of trisiloxane surfactant solutions for spreading on low-energy surfaces has been stressed.[5,8] For surfactants of the oligoethylene glycol type, this turbid two-phase state is usually adjusted by temperature variation.[9–13] Extensive experiments have demonstrated that the spreading behaviour of the polydisperse Silwet L77 is nearly independent of the temperature and the phase state of the solution.[5] Results for trisiloxane surfactant–additive mixtures support this finding.[14] It could be shown that certain additives generate non-turbid solutions and simultaneously increase the spreading rate. Furthermore, the spreading rates of aqueous solutions of defined oligoethylene-glycol-modified hydrocarbon surfactants (C_iE_j) 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. A recent paper[15] focused on the general ability of certain trisiloxane-based surfactants to form

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† Part 2 was published in *Appl. Organometal. Chem.* **13**, 201–208 (1999).

Contract/grant sponsor: Deutsche Forschungsgemeinschaft; Contract/grant number: WA 1043 / 1–2.

CCC 0268–2605/99/090621–10 $17.50

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

Compd.	Colour	Purity (%GC)	Contamination (%)	
			Si-containing	Without Si
EO_3	Colourless	$\gg$99		
EO_4	Colourless	$\gg$99		
EO_5	Colourless	99		1.0
EO_6	Pale yellow	97.5	1 (EO_5 type)	1.5
EO_7	Pale yellow	96	1.5 (EO_6 type)	2.5
EO_8	Yellow	95	1.5 (EO_6 type)	3.5
EO_9	Pale brown (Pt)	90	10 (EO_7+EO_8 types)	

vesicles as an essential prerequisite for superspreading.

These contrary findings clearly demonstrate that a comprehensive understanding of the superspreading phenomenon has not been reached.[16] A better understanding of the basic principles necessitates the investigation of sufficiently pure trisiloxane-based individual compounds. We showed[17] 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. Recently[18] we described the synthesis of individual components of Silwet L77 bearing three to nine oligoethylene glycol units attached to the trisiloxane block. The derivative bearing six ethylene glycol moieties spreads faster and to larger areas than all the others at 26 °C on a hydrophobic silicon wafer surface. The experiments also proved that for single compounds a pronounced temperature and therefore phase-type dependence of the spreading rate exists (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999). For dispersed (two-phase, 2Φ) systems close to the transition temperature (T_c) from the lamellar phase (L_α) to the two-phase state (2Φ), the highest initial spreading rates can be expected.

Since this rule does not hold for the mixture Silwet L77, a systematic investigation of less complex mixtures could answer the question of whether it is possible to distinguish between single compounds and defined mixtures. Therefore the purpose of this study was to investigate the dependences of spreading rate and phase behaviour on the composition of trisiloxane surfactant mixtures.

2 MATERIALS AND METHODS

2.1 Materials

The synthesis of defined 1,1,1,3,5,5,5-heptamethyltrisiloxanyl (MD*M) derivatives of general structure $[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_nOCH_3$, $n = 3$–9, has been outlined in an earlier paper.[18] Table 1 summarizes the colours, purities and product compositions of the siloxanyl-modified oligoethylene glycols.[18]

For the spreading experiments a low-energy silicon wafer surface was prepared. After ultrasonication in ethanol, methylene chloride and diethyl ether wafer pieces were placed in an oxidizing solution consisting of 39 parts of conc. H_2SO_4, 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 wafer pieces were rinsed with diethyl ether, ethanol and twice-distilled water.

Prior to the experiments the surface energies of the wafers were 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 in Table 2 represent the mean values of at least four measurements. Deviations larger than $\pm 1°$ for single measurements were not observed. The data for the strictly non-polar alkanes ($\gamma_{lv} = \gamma_{lv}^{LW}$) were used to calculate γ_{sv} (Neumann,[19] Eqn [1]) and γ_{sv}^{LW} (Good,[20] Eqn [2]). The good agreement between the corresponding γ_{sv} and γ_{sv}^{LW} values indicates the non-polar character of the surfaces (Eqns [1],[2]).[17,21]

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

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

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

	Liquid			
	H_2O	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$
γ_{lv} (mN/m) (20°C)	72.6	26.6	27.3	27.6
θ (°)	91	29	34	38
γ_{sv} (mN m^{-1} (Neumann)		23.2	23.7	24.0
$\gamma_{sv}{}^{LW}$ (mN m^{-1} (Good)		23.0	23.6	23.9

2.2 Methods

The general procedure of the spreading experiments has been described in earlier papers (Ref. 18, see also R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999). Spreading experiments on the surface of the silicon wafers have been carried out in laboratories kept at 15 ± 0.5 °C (29 ± 1% relative humidity) and 23 ± 0.5 °C (52 ± 1% relative humidity) respectively. Prior to the experiments, chemicals and equipment had been stored under these conditions for at least 12 h. The hydrophobic 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 hand-shaken for 2 min and afterwards ultrasonicated for 2 min in a water bath thermostated to actual laboratory temperature. A microsyringe was used to deposit 10 µl of the surfactant solutions on the trimethylsilyl-modified silicon wafers.

High-temperature experiments were carried out on a heating plate kept at 40 ± 2 °C and 30 ± 2% relative humidity. The temperature of freshly prepared surfactant solutions was separately adjusted in a water bath at 40 °C. Afterwards they were shaken and ultrasonicated in a thermostated water bath (40 °C, 2 min). In order to avoid temperature changes in the solutions the drops were deposited within a few seconds on the wafer surface.

Explorative experiments showed that medium relative humidities <90% did not influence significantly the spreading results on the very low-energy surface. We cannot exclude certain high-temperature evaporation effects at drop edges. Therefore, primarily the data sets for single components and mixtures measured at one temperature and relative humidity are compared However, a comparison of the relative orders of compounds and mixtures at different temperatures discloses substantial information on the nature of the spreading process.

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 point (spreading time = 0) was critical. Drops (10 µl) of a 1 wt% solution of the triethylene glycol derivative EO_3 did not spread, and covered equilibrium areas of 11.5 mm^2 (15 °C), 14.1 mm^2 (23 °C) and 16.6 mm^2 (40 °C) respectively. These areas defined the starting points of the spreading experiments. For a given time the mean spreading areas have been 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 samples for the phase investigations were prepared by mixing the surfactants with twice-distilled water in glass test-tubes. After mixing, the solutions were subject 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 could be determined in this way with an accuracy of ± 0.1 °C. Birefringence indicated the presence of anisotropic liquid-crystalline phases. Flow birefringence was observed by stirring.

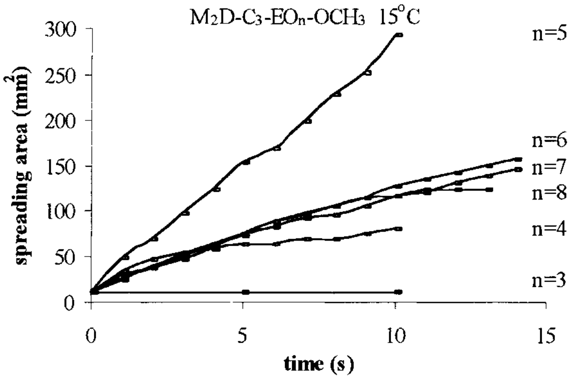

Figure 1 Time-dependent spreading areas for defined oligoethylene glycol derivatives at 15 °C ($c = 1$ wt%).

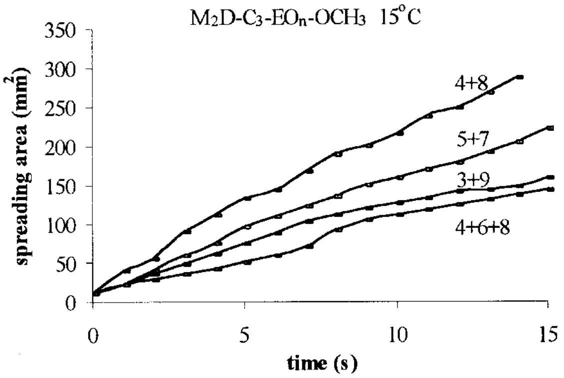

Figure 3 Time-dependent spreading areas for equimolar mixtures of oligoethylene glycol derivatives similar to EO_6 at 15 °C ($c = 1$ wt%).

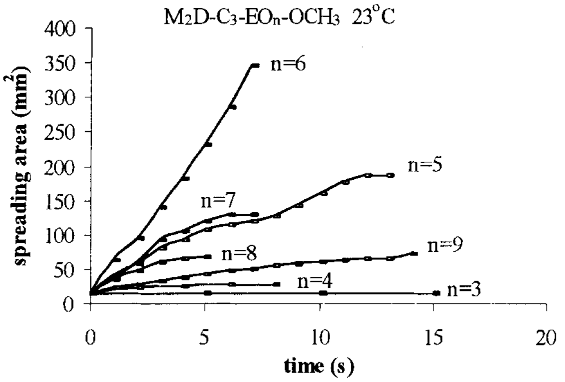

Figure 2 Time-dependent spreading areas for defined oligoethylene glycol derivatives at 23 °C ($c = 1$ wt%).

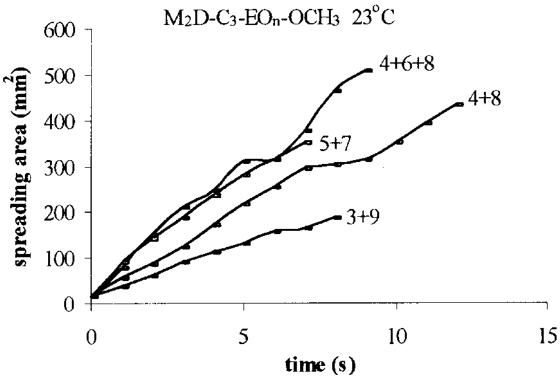

Figure 4 Time-dependent spreading areas for equimolar mixtures of oligoethylene glycol derivatives similar to EO_6 at 23 °C ($c = 1$ wt%).

3 RESULTS

Figures 1 and 2 describe the temperature dependence of the spreading areas for 1 wt% solutions of the single compounds. The lower the temperature the shorter the oligoethylene glycol chain necessary in order to reach the maximum spreading areas and rates (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999).

Figures 3 and 4 depict spreading data for binary and ternary surfactant systems at 15 °C and 23 °C (1 wt%). The common oligoethylene glycol chain length of all equimolar mixtures is six. The data prove that at 23 °C the binary mixture EO_{5+7} spreads considerably faster than the corresponding single component EO_6 (see Fig. 2). Further, a decreasing chain length difference between the two compounds accelerates the spreading process. These mixtures spread significantly more slowly at 15 °C. A noticeable exception is the mixture EO_{4+8}. In this particular case a T_c very close to the spreading temperature causes a less pronounced reduction in the ability to spread.

In Figs 5 and 6 the corresponding area vs time curves for equimolar mixtures with average oligoethylene glycol chain lengths of four, five and seven are shown. At 15 °C the mixture EO_{3+7} is the fastest spreader. It imitates the the fastest single spreader, EO_5. The apparently minor chain length reduction to EO_{3+6} already considerably reduces the ability to spread. At 23 °C only minor differences between the mixtures were found. None of these mixtures is optimized at this temperature.

Figure 7 summarizes the data of those single components (R. Wagner, Y. Wu, G. Czichocki, H.

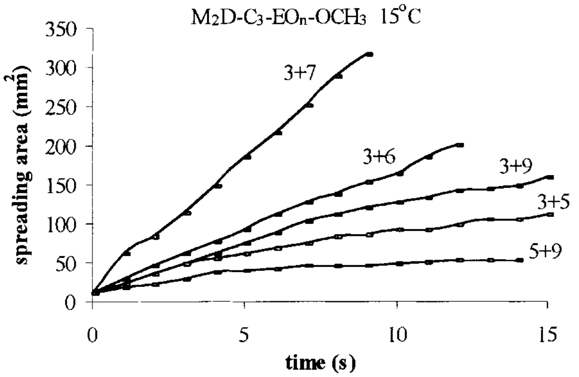

Figure 5 Time-dependent spreading areas for equimolar mixtures of oligoethylene glycol derivatives similar to EO_4, EO_5 and EO_7 at 15 °C (c = 1 wt%).

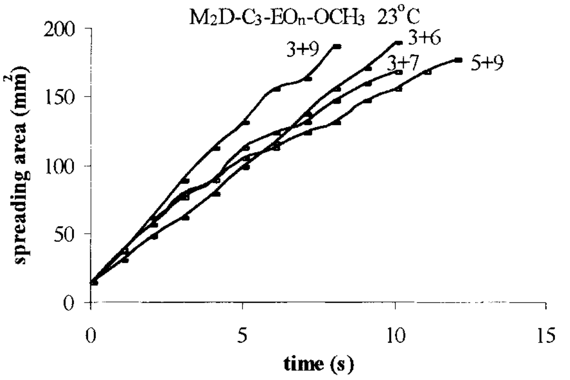

Figure 6 Time-dependent spreading areas for equimolar mixtures of oligoethylene glycol derivatives similar to EO_4, EO_5 and EO_7 at 23 °C (c = 1 wt%).

v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999) and equimolar mixtures which spread at 40 °C. Effective spreaders are EO_8 and EO_{7+9}. For shorter-chained single components and mixtures, very slow spreading was observed at 1 wt% concentration. Clearly, at higher temperatures a very narrow window for rapid spreading exists. Probably, two-phase systems decompose under these conditions macroscopically and lose the ability to spread.

Figures 8 and 9 describe the concentration dependence of the initial spreading rate for the single components. The initial spreading rates have been calculated from the slopes of the area vs time curves. As expected (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**,

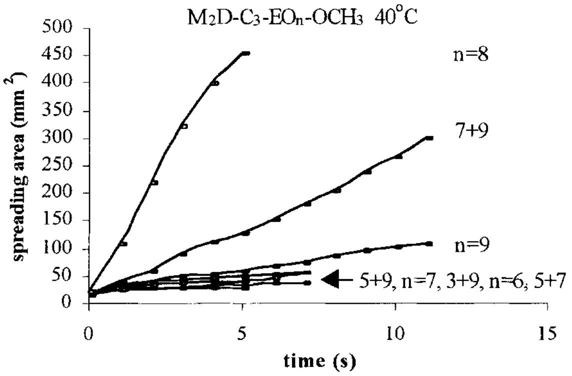

Figure 7 Time-dependent spreading areas for single components and equimolar mixtures of oligoethylene glycol derivatives at 40 °C (c = 1 wt%).

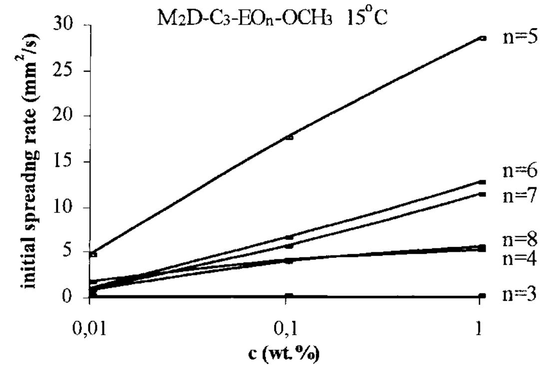

Figure 8 Derivatives EO_3 to EO_9: concentration dependence of the initial spreading rate at 15 °C.

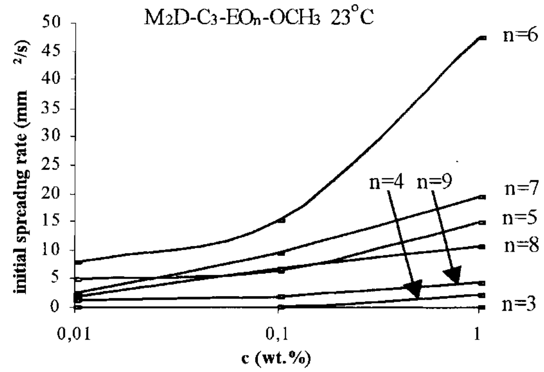

Figure 9 Derivatives EO_3 to EO_9: concentration dependence of the initial spreading rate at 23 °C.

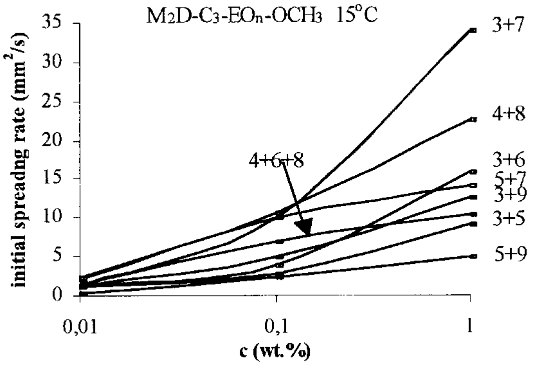

Figure 10 Equimolar mixtures of oligoethylene glycol derivatives: concentration dependence of the initial spreading rate at 15 °C.

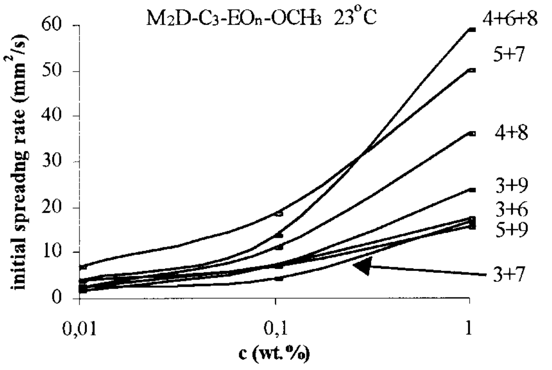

Figure 11 Equimolar mixtures of oligoethylene glycol derivatives: concentration dependence of the initial spreading rate at 23 °C.

201–208 (1999), EO_6 is the fastest spreader at 23 °C, whereas at 15 °C the shorter-chained derivative EO_5 spreads faster than all the other compounds.

Figures 10 and 11 summarize the corresponding initial spreading rates for the equimolar mixtures. At 23 °C the highest initial spreading rates are found for mixtures imitating EO_6. At 15 °C the mixture EO_{3+7} is the fastest spreader. Although not imitating EO_5, the mixture EO_{4+8} spreads rapidly.

Figure 12 depicts the initial spreading rates for those single components (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999) and equimolar mixtures which spread at 40 °C. As already outlined, EO_8 and EO_{7+9} are effective spreaders.

Figures 13 and 14 summarize the 1 wt% initial

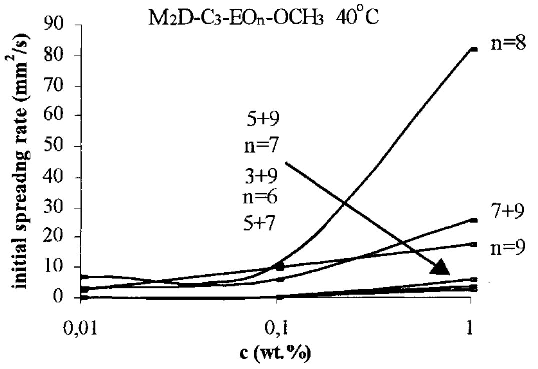

Figure 12 Single components and equimolar mixtures of oligoethylene glycol derivatives: concentration dependence of the initial spreading rate at 40 °C.

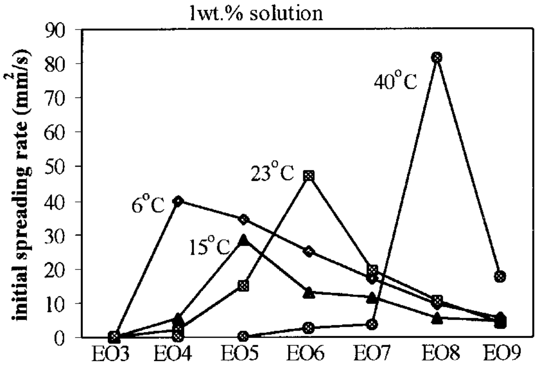

Figure 13 Derivatives EO_3 to EO_9: temperature dependence of the initial spreading rate ($c = 1$ wt%). Data for 6 °C are included from R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999).

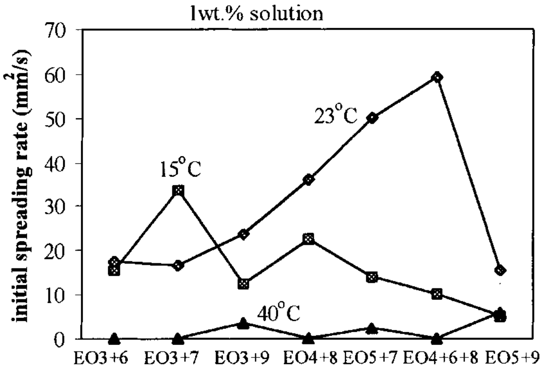

Figure 14 Equimolar mixtures of oligoethylene glycol derivatives: temperature dependence of the initial spreading rate ($c = 1$ wt%).

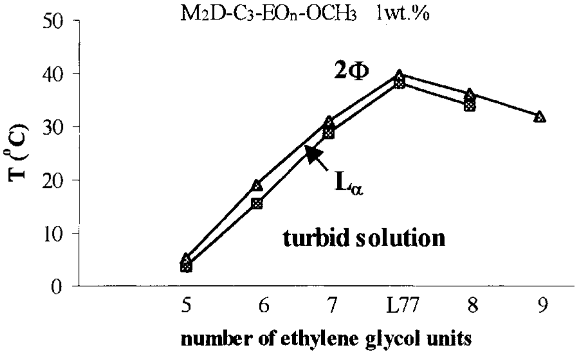

Figure 15 Phase transition temperatures as a function of the oligoethylene glycol chain length ($c = 1$ wt%).

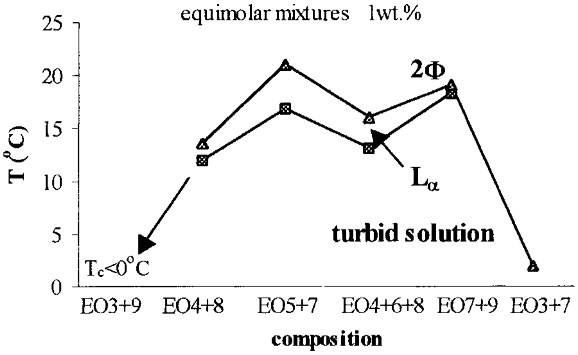

Figure 16 Phase transition temperatures as a function of the composition of the surfactant mixture $c = 1$ wt%.

spreading rates of those single components and equimolar mixtures which have been investigated at 15 °C, 23 °C and 40 °C. For the single components (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999) as well as the mixtures, the optimized chain length is a function of the temperature.

Figures 15 and 16 summarize the phase transition temperatures of single compounds and mixtures at a concentration of 1 wt%. The general pattern of the phase behaviour of the single compounds has been outlined earlier (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999) and agrees qualitatively with that for the commercially available polydisperse trisiloxane superspreaders.[10,11]

All single surfactant solutions are more or less turbid at low temperatures and show birefringence. On increasing the temperature the solutions became increasingly transparent and showed the texture of a lamellar phase between crossed polarizers. Typically, the solutions were iridescent, bearing colour stripes ranging from red to blue. We assume by analogy with related hydrocarbon-[12] and siloxane-based compounds (Refs 10, 11; see also H. v. Berlepsch and R. Wagner, *Prog. Colloid Polym. Sci.*, **111**, 107–112 (1998) that the mixtures are dilute dispersions of bilayer aggregates (L_α phase). Upon increasing the temperature the samples become cloudy but isotropic and show complete phase separation after some hours. This two-phase state is signated as 2Φ and the liquid–liquid insolubility boundary is specified as cloud point T_c. An intermediate-flow birefringent-sponge phase (L_3 phase) could not be identified reliably for 1 wt% solutions (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999).

For surfactant mixtures we found the similar sequence, lamellar phase (L_α) $\rightarrow$ two phases (2Φ).

4 DISCUSSION

4.1 Composition of surfactant mixtures

Recently we showed (Ref. 18; see also (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999) that rapid spreading of defined oligoethylene-glycol-modified trisiloxane surfactants on a non-polar, low-energy surface is bound to the existence of a microdispersed two-phase state (2Φ). Rapid spreading occurs if the individual-phase transition temperature (T_c) lamellar phase (L_α) $\rightarrow$ two-phase state (2Φ) is slightly below the actual spreading temperature. This finding implies that, depending on the spreading temperature, different individual molecules show the highest initial spreading rates.

This rule is not valid for the surfactant mixture Silwet L77. These solutions spread well at 6 °C as well as at 40 °C. Rapid spreading is reported for temperatures as high as 55 °C.[5] Additionally, a correlation between spreading rate and phase state does not exist.

From this background we investigated the influences of temperature and varying mixture compositions on the spreading rates.

Figures 1, 2 and 7 prove that for 1 wt% single-surfactant solutions a pronounced temperature dependence of the initial spreading rate exists. The higher the temperature, the longer the oligoethylene glycol chain necessary for an optimized spreading process. The relationship outlined above between T_c (Fig. 15) and spreading rate at a defined spreading temperature holds. It is important to note that a concentration reduction alters neither the sequence of the surfactants nor the expected[18] concentration dependence of the initial spreading rates (Figs 8, 9 and 12). Rapid spreaders remain superior at low concentrations and the lower the concentration, the lower the initial spreading rate. Minor scatterings at the concentration $c = 0.01$ wt% are due to the very low absolute initial spreading rates.

The behaviour of mixtures deviates markedly from that of the single compounds. One of the most exciting findings during the course of these investigations was that for a given temperature the fastest spreading single compound can be substituted by mixtures mimicking its optimized oligoethylene glycol chain length.

The equimolar mixtures EO_{3+9}, EO_{4+8} and EO_{5+7} (Figs 4 and 11) imitate the single compound EO_6, which is the fastest spreader at 23 °C (Figs 2 and 9). These mixtures spread substantially faster than the corresponding single compounds. The steepest relative spreading rate increase was observed for the system EO_{3+9}: Here the mixture spreads 6.5 times faster than EO_9 (1 wt%). This finding means that the mixture of two extremely poor spreaders yields a very fast system. The mixtures EO_{4+8} and EO_{5+7} spread 3.5 and 2.5 times faster than the corresponding fastest single compounds EO_8 and EO_7 respectively. It is important to note that the order of the absolute spreading rates $EO_{3+9} < EO_{4+8} < EO_{5+7}$ is the inverse of that of the relative spreading rate increases. Clearly, a broadening of the distribution partially counteracts the adjustment of an optimized chain length.

On the other hand an addition of EO_6 to the binary mixture EO_{4+8} narrows the distribution and makes the ternary mixture EO_{4+6+8} superior (Figs 4 and 11).

A comparison of the binary mixtures EO_{3+9} and EO_{3+6} at 23 °C emphasizes the dominance of the average chain length (Figs 4, 6 and 11). The latter mixture spreads much more slowly despite containing 50% of the fast-spreading hexaethylene glycol derivative. Collective properties replace individual ones.

From the background of the dominance of the average chain length, the superior properties of EO_{7+9} at 40 °C and EO_{3+7} at 15 °C were expected. These mixtures imitate the optimized spreaders EO_8 and EO_5

The systems react sensitively to shifts in chain length, however. At 15 °C the apparently minor, shift from EO_{3+7} to EO_{3+6} yields a dramatic reduction in the initial spreading rate (Figs 6 and 11).

Despite the loss of the individual properties demonstrated above, the pronounced preference of binary mixtures for narrow temperature windows is immediately reminiscent of single compounds. Silwet L77 behaves differently.[5]

4.2 Phase transition temperature T_c

The second fundamental property of single compounds is the close relationship of initial spreading rate and phase behaviour (R. Wagner, Y. Wu, G. Czichocki, H. v. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organometal Chem.*, **13**, 201–208 (1999).

The investigations show that there is no qualitative difference between the phase behaviour of single compounds (Fig. 15) and that of equimolar mixtures (Fig. 16). On increasing the temperature, turbid solutions become transparent initially, form lamellar phases (L_α) and finally separate into two phases (2Φ). The actual transition temperature T_c is a function of the composition.

For a given average chain length, increasing length and T_c differences between the two components substantially reduce the phase transition temperatures (see EO_{3+9}, EO_{4+8} and EO_{5+7}). The chain length difference is the major impact factor. T_c of EO_{3+9} (<0 °C) is much lower than that of EO_{3+7} (5.1 °C). Here the extreme chain length difference of six units for EO_{3+9} overrules the higher T_c of EO_9 (EO_9 32 °C, EO_7 31.5 °C) and even the increased average chain length of this mixture.

The data in Figure 16 prove that the correlation between initial spreading rate and phase state is superposed by an argument based on mixture properties. Within a series of mixtures of identical number of participating compounds and average chain length, the correlation between initial spreading rate and T_c holds. At 23 °C the equimolar mixture EO_{5+7} spreads much faster than EO_{4+8} and EO_{3+9} (Fig. 11). T_c of EO_{5+7} (19.0 °C) is only slightly below the spreading temperature. The corresponding phase transition temperatures of EO_{4+8} (14.4 °C) and EO_{3+9} (<0 °C) are much lower. The tendency for macroscopic phase separation is more pronounced.

It is advantageous to increase the number of participating compounds with maintenance of the optimized chain length. The addition of the hexaethylene glycol derivative to the binary mixture EO_{4+8} yields a ternary mixture with a slightly higher T_c [EO_{4+8} (14.4 °C) $\rightarrow$ EO_{4+6+8} (17.2 °C)] but considerably increased initial spreading rate (Fig. 5b). The quality of the ternary system becomes clear in a comparison with the binary mixture EO_{5+7}, EO_{4+6+8} spreads faster despite a significantly lower T_c.

It is not advantageous to deviate from the temperature-dependent optimized chain length with maintenance of the number of participating compounds. Mixture EO_{3+7} spreads more slowly at 23 °C than EO_{3+9}, EO_{4+8} and EO_{5+7} (Figs 6 and 11). An apparently reasonable explanation is the low T_c of EO_{3+7} compared with those of EO_{4+8} and EO_{5+7}. Intriguingly, T_c of EO_{3+9} is lower than that of EO_{3+7}. Clearly the maintenance of the optimized chain length is more important than a T_c close to the spreading temperature.

Nevertheless, in certain situations a T_c close to the actual spreading temperature can substantially increase the initial spreading rate. At 15 °C EO_5 (Figs 1 and 8) and its binary imitation EO_{3+7} (Figs 5 and 10) are the fastest spreaders. Mixtures like EO_{5+9}, EO_{3+9}, EO_{5+7}, and EO_{3+6} do not possess an optimized average chain length and spread markedly more slowly (Fig. 10). However, the mixture EO_{4+8} spreads substantially faster than all the other non-optimized mixtures and is the only one that comes close to the spreading behaviour of EO_5 and EO_{3+7}. Perhaps this apparently unmotivated spreading behaviour is due to the phase state. At 15 °C, EO_{4+8} is just above the lamellar region in the two-phase state (2Φ) and very close to T_c. In this particular case the advantage of an almost optimized T_c partially compensates for the 'wrong' chain length.

It becomes clear that for binary and ternary mixtures a correlation between initial spreading rate and phase behaviour does not exist. Meaningful relations are restricted to mixtures of the same average chain length and possibly the same level of complexity.

Although not well understood, it is a characteristic aspect that for solutions of the optimized chain length extreme differences between T_c and the spreading temperature are tolerated (see EO_{3+9}). Concerning T_c, the behaviour of these mixtures is similar to that of Silwet L77.

4.3 Conclusion

The spreading behaviour of equimolar binary and ternary mixtures falls between that of single compounds and Silwet L77. The pronounced temperature dependence of the initial spreading rates is a well-documented property of single surfactants. The non-existence of a relationship between T_c and initial spreading rate is similar to Silwet L77 behaviour.

The adjustment of an optimized average chain length is the major means to enhance the spreading process. However, an increase in the chain length difference between the two compounds in binary mixtures gradually reduces the initial spreading rate.

Nevertheless, for chain-length-optimized mixtures, considerable differences between T_c and the actual spreading temperature can be accepted. On the other hand, a T_c close to the actual spreading temperature substantially increases the spreading rates of less chain-length-optimized mixtures.

Silwet L77 contains the single components in non-equimolar proportions. Therefore an investigation of less complex non-equimolar mixtures is necessary. The question of the dependence of the spreading rate of trisiloxane surfactant solutions on the chemical structure and surface energy of solid materials is of immediate practical importance. Both topics will be the subject of a separate paper.

Acknowledgement The project 'Polyhydroxylated silicon compounds' is supported by the Deutsche Forschungsgemeinschaft (Reg. no. WA 1043/1–2).

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