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Silicon-Modified Carbohydrate Surfactants: IV. The Impact of Substructures on the Wetting Behaviour of Siloxanyl-Modified Carbohydrate Surfactants on Low-Energy Surfaces

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The siloxanyl-modified carbohydrate surfactants investigated consist of the four structural elements: (1) siloxanyl moiety; (2) spacer; (3) carbohydrate unit; and (4) modifying element. By static surface tension (γ_{lv}, σ) and wetting tension ($\gamma_{sv} - \gamma_{sl}$, α) measurements the contact angles of aqueous surfactant solutions above the critical micelle formation concentration (cmc) on nonpolar perfluorinated surfaces (FEP® plate) were determined. Although the siloxanyl units were found to have a high capacity to level out the interfacial properties, both surface tension and wetting tension react independently to defined changes in the chemical structure of the surfactant molecules. The results of spreading experiments on polypropylene show good correlation with the dependences found by wetting measurements. © 1997 John Wiley & Sons, Ltd.

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1 INTRODUCTION

In the framework of the concept of a ‘surfactant-enhanced spreading’[1] the exceptional property of aqueous solutions of certain siloxane surfactants is their ability to wet rapidly low-energy surfaces (i.e. polyethylene, polypropylene, layers of natural waxes). Due to this superspreading property they are extensively used as adjuvants in plant protection formulations.[2,3] The siloxane surfactants lower the surface tension of the formulations to values below 25 mN m^{-1}. Even wax-covered, low-energy leaf surfaces can be wetted by these formulations. The capillary forces of the stomata are overcome and the biologically active principle can penetrate directly into the interior[4] (stomata infiltration). The slower and less effective penetration through the cuticula can be bypassed.[5]

Since not every siloxane surfactant is a superspreader on low-energy surfaces,[1] intensive studies have been carried out to define the structural factors and understand the mechanisms responsible for this effect. The results can be summarized as follows.[1,6–9]

(a) siloxane structures are necessary for the occurence of this superspreading effect;
(b) neither hydrocarbon-based nor perfluorinated surfactants are superspreaders on low-energy surfaces;
(c) the structure of the trisiloxanyl unit (hammer-like, linear) is not a critical parameter as long as surfactant bilayers can be formed;
(d) the existence of a dispersed surfactant-rich phase is crucial;

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(e) bulky hydrophilic substructures (long ethylene oxide chains) inhibit or prevent spreading by inhibiting bilayer formation;
(f) high air humidity or the presence of water deposited on the solid surface accelerates superspreading;
(g) the surface tension of the siloxane surfactants is not the only driving force of the superspreading process;
(h) extreme low-energy surfaces (PTFE; long-chained alkyltrichlorosilane-treated surfaces) are not wetted;
(i) low local surface tensions and solid/liquid interfacial tensions are necessary;
(j) equilibrium between surfactant–surfactant and surfactant–solid surface interactions is very important.

Although analysis shows that, together with chemical, geometrical and kinetic influences [points (a) to (e)], energetically founded ones [(b), (f) to (j)] govern the superspreading process, attention has not been focused on correlations between energetic parameters and spreading data.

Recently published results[10] concerning dynamic surface tension and dynamic interfacial tension measurements (aqueous surfactant solutions vs n-alkanes) suggest that bulk diffusion coefficients of superspreaders are one order of magnitude higher than those of conventional surfactants. Unfortunately such experiments cannot simulate the real situation in the vapour/aqueous surfactant solution/insoluble solid material system.

In earlier papers, we described the synthesis of siloxanyl-modified carbohydrate surfactants.[11–13] Essentially these surfactants consist of four substructures: (1) siloxanyl moiety; (2) spacer; (3) carbohydrate unit; and (4) modifying element. Each of these four elements can be varied, within the framework of the synthetic concept, independently and over a wide range of concrete structures. In contrast to the ethylene oxide derivatives investigated so far,[1] the sensitive aspect of molecular weight distributions plays no role. This opens up the possibility of studying the influence of very different structures on the interfacial behaviour in a systematic series.

In an attempt to systematize the impacts of surfactants chemical structure and molecular geometry on the wetting and spreading behaviour, it is the main object of this paper to quantify the influences of different substructures of siloxane surfactants on the energetic balance at the liquid/vapour and solid/liquid interfaces under equilibrium conditions. It will be demonstrated that combined surface and wetting tension measurements on a nonpolar perfluorinated surface give access to the effects of defined substructures in siloxane surfactant molecules. Finally it will be shown that the tendencies of the wetting data correspond well to those of practical spreading experiments on polypropylene.

2 MATERIALS AND METHODS

2.1 Materials

The synthesis and chemical characterization of the siloxanyl-modified carbohydrate surfactants has been described in detail in earlier papers of this series.[11,12] Schemes 1–3 demonstrate basic reaction principles.

As their general structure consists of a siloxanyl moiety (si), spacer (sp), carbohydrate unit (ch) and modifying element (mo) (Fig. 1), we investigated four series of substances. In each series one structural element was varied systematically (Figs 2–5).

We also tested aminosiloxanes (compounds. **25**, **26** and **27**, Fig. 6) which served as key intermediates in the reaction sequences in Scheme 1. The extensively used Silwet L-77[8] (compound **28**, Fig. 6; Union Carbide) has also been investigated as a reference substance. The siloxanyl-modified carbohydrate surfactants **29** and **30** (Fig. 7) have been used for comparative purposes.

2.2 Methods

To determine the critical micelle formation concentration (cmc), the surface tensions of diluted aqueous surfactant solutions were measured at room temperature according to the De Noüy ring method.[14] The data were corrected according to Harkins and Jordan.[15] A Krüss tensiometer, model K10T, was used.

The adsorption behaviour at the liquid/vapour interface was characterized by the Frumkin isotherm[16] (Eqns [1a] and [1b]). It was found that the data fit best to this type of isotherm, which includes surfactant–surfactant and surfactant–solvent interactions by definition. It has to be stated that so far no prediction is possible which isotherm describes best the behaviour of a given surfactant in solution.[17]

$$c_{b_F} = \frac{\Omega_F}{n(1-\Omega_F)^n}\exp(-2a\Omega_F) \qquad [1a]$$

$$\pi = -RT\,\Gamma_{\infty F}(\ln(1-\Omega_F)+a\Omega_F^{2}) \qquad [1b]$$

$c =$ bulk concentration;
$b_F =$ a term depending on the adsorption equilibrium constant;
$\pi =$ surface pressure $\sigma_0 - \sigma$;
$\Gamma_{\infty F} =$ saturation adsorption;
$\Omega_F =$ $\Gamma/\Gamma_{\infty F}$ surface coverage of the surfactant;
$a =$ interaction parameter, describing the deviation from the ideal (Langmuir) behaviour by possible surfactant–surfactant and surfactant–solvent interactions in the adsorption layer;
$n =$ index describing the displacement of the solvent by other molecules.

The area occupied by a surfactant molecule in the adsorption layer was calculated by Eqn [2]:

$$A = \frac{1}{\Gamma_{\infty F}\cdot N_L} \qquad [2]$$

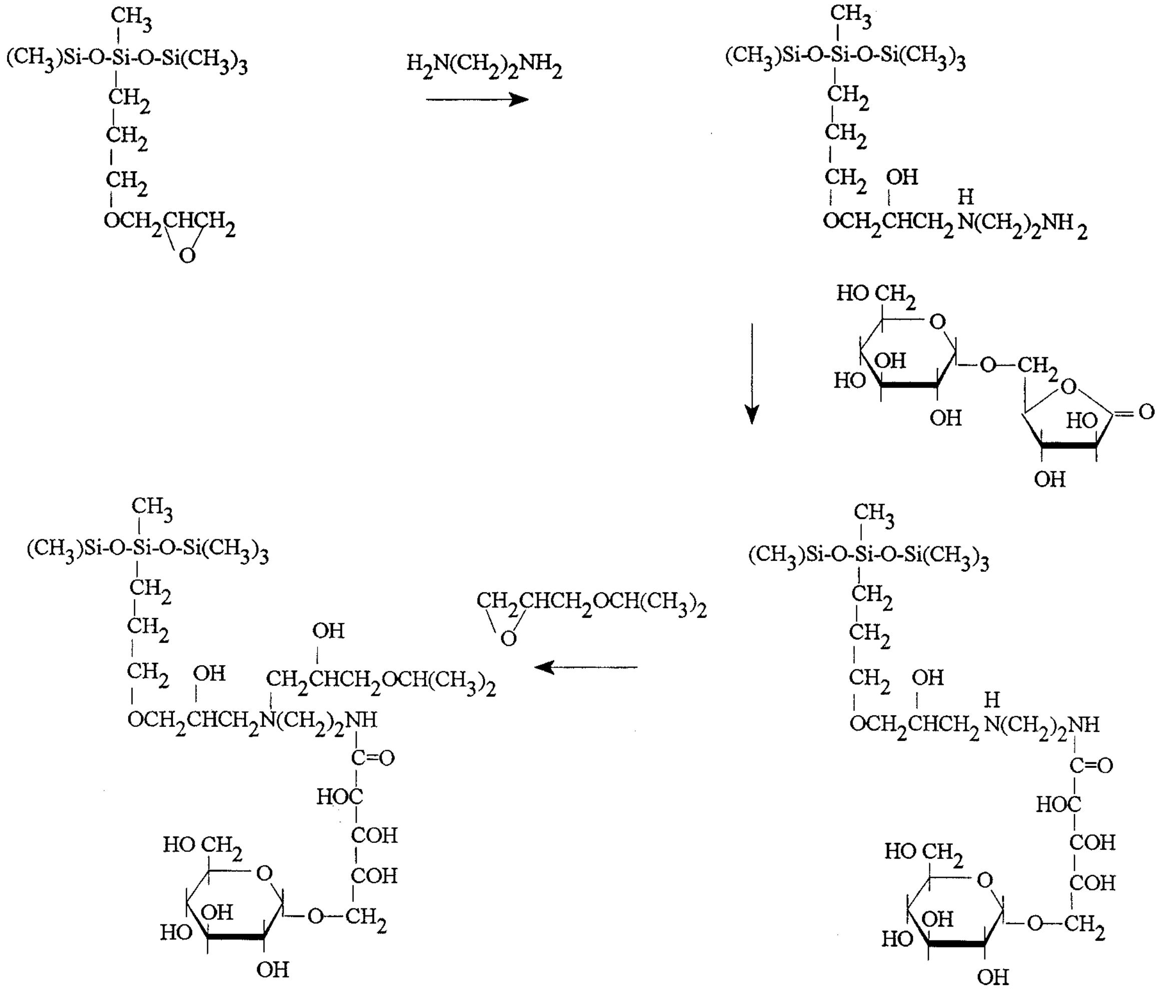
where N_L = Loschmidt constant

The standard free adsorption energy $\Delta G^{\ominus}$ describes the tendency of the surfactant molecules to occupy places at the surface and was calculated by Eqn [3]:

$$\Delta G^{\ominus} = RT\ \ln\ (M_v - b_F) \qquad [3]$$

where M_v = molar volume (22.4 l mol^{-1}).

The behaviour of a liquid on a plane solid



Scheme 1

surface is determined by the equilibrium of three forces: (1) liquid/vapour interfacial tension (surface tension of the liquid γ_{lv} or σ); (2) solid/vapour interfacial tension (solid surface tension γ_{sv}); and (3) solid/liquid interfacial tension (γ_{sl}) (Fig. 8). It finds its expression in the well-known Young equation[18] (Eqn [4]):

$$\frac{\gamma_{sv}-\gamma_{sl}}{\gamma_{lv}}=\frac{\alpha}{\sigma}=\cos\theta \qquad [4]$$

where α = wetting tension (Fig. 8).

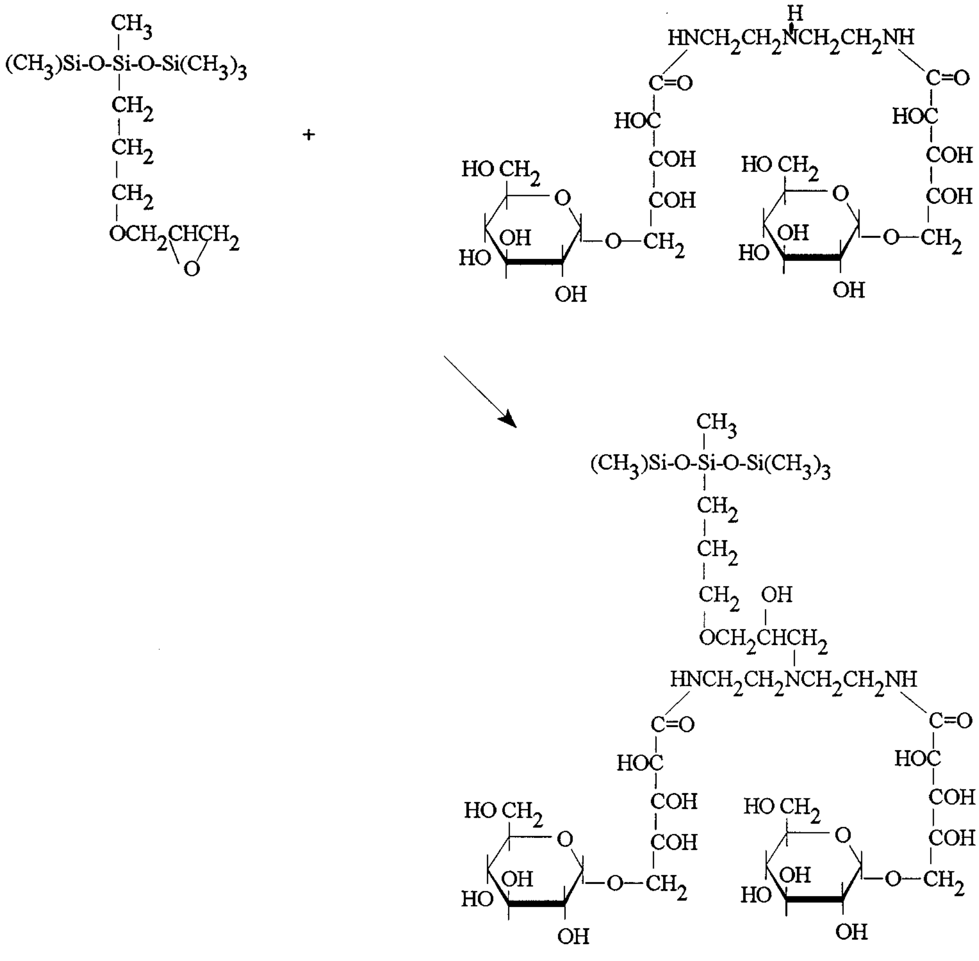
The contact angles of aqueous surfactant solutions with $c > c_{cmc}$ (measuring concentration usually 10^{-3} mol l^{-1}; for surfactants with cmc $> 10^{-3}$ mol l^{-1} the concentration was increased to 2×10^{-3} mol l^{-1}) on nonpolar FEP® plates (tetrafluoroethylene–hexafluoropropylene-copolymer; DuPont) were determined according to Eqn [4] by measuring independently surface tension γ_{lv} (ring method) and wetting tension α (Wilhelmy method).[19] Each measurement was carried out at 20 °C.

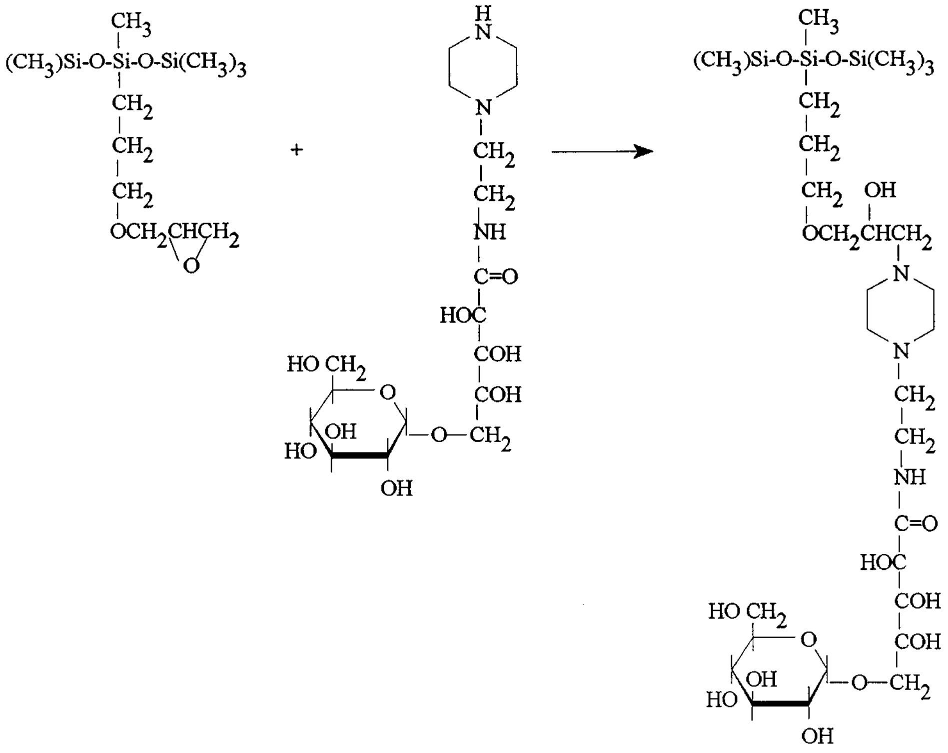
To measure the wetting tension, an FEP® plate of defined width and thickness was dipped stepwise (0.2 cm) into the surfactant solution with an accuracy of 0.001 cm. The force (p) measured correlates with α (Eqn [5])

$$p=u\alpha+(-)\rho g d b x_e \qquad [5]$$

where
u = perimeter of the FEP® plate;
ρ = liquid density;
g = gravitational constant;
d = thickness of the plate;
b = width of the plate;
x_e = immersion depth of the plate.

After every movement of the plate we measured


Scheme 2



Scheme 3

the force immediately and also after 5 min (compound **11** after 15 min). This time was found to be necessary for the system to reach an equilibrium state of wetting. By plotting the 5(15)-min values of the force p against the immersion depth x_e, after extrapolation to $x_e = 0$ the wetting tension α is obtained.

The solid surface tension γ_{sv} of FEP® has been determined from surface tension γ_{lv} and contact angle Θ (calculated from γ_{lv} and α) measurements on a series of nonpolar n-alkanes. The approaches of van Oss[20] (Eqn [6]) and Neumann[21] (Eqn [7]) were applied.

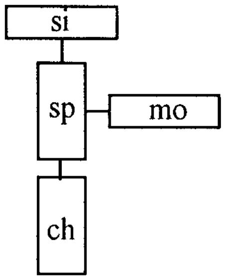


Figure 1 General structure of the siloxanyl-modified carbohydrate surfactants.

$$1+\cos\theta=2\sqrt{\frac{\gamma_{sv}^{LW}}{\gamma_{lv}}} \qquad [6]$$

$$\cos\theta=\frac{(0.015\gamma_{sv}-2)\sqrt{\gamma_{sv}\cdot\gamma_{lv}}+\gamma_{lv}}{\gamma_{lv}(0.015\sqrt{\gamma_{sv}\cdot\gamma_{lv}}-1)} \qquad [7]$$

The interfacial tension γ_{sl} was calculated from the γ_{sv}–α relationship (see Eqn [4]).

In order to analyse possible correlations between surfactant structure and type or emerging forces, we determined the Lifshitz–van der Waals portions of the surface tension[22] (γ_{lv}^{LW}) (Eqn [8]) and solid/liquid interfacial tension[23] (γ_{sl}^{LW}) (Eqn [9]):

$$\gamma_{lv}^{LW}=\left[\frac{\gamma_{lv}\cdot(1+\cos\theta)}{2\sqrt{\gamma_{sv}^{LW}}}\right]^2 \qquad [8]$$

$$\gamma_{sl}^{LW}=\gamma_{sv}^{LW}+\gamma_{lv}^{LW}-2\sqrt{\gamma_{sv}^{LW}\cdot\gamma_{lv}^{LW}} \qquad [9]$$

The polar portions ($\gamma_{lv}^{+/-}$) and ($\gamma_{sl}^{+/-}$) were calculated according to Fowkes approach[24] (Eqn [10]):

$$\gamma_{lv}=\gamma_{lv}^{LW}+\gamma_{lv}^{+/-} \qquad [10]$$

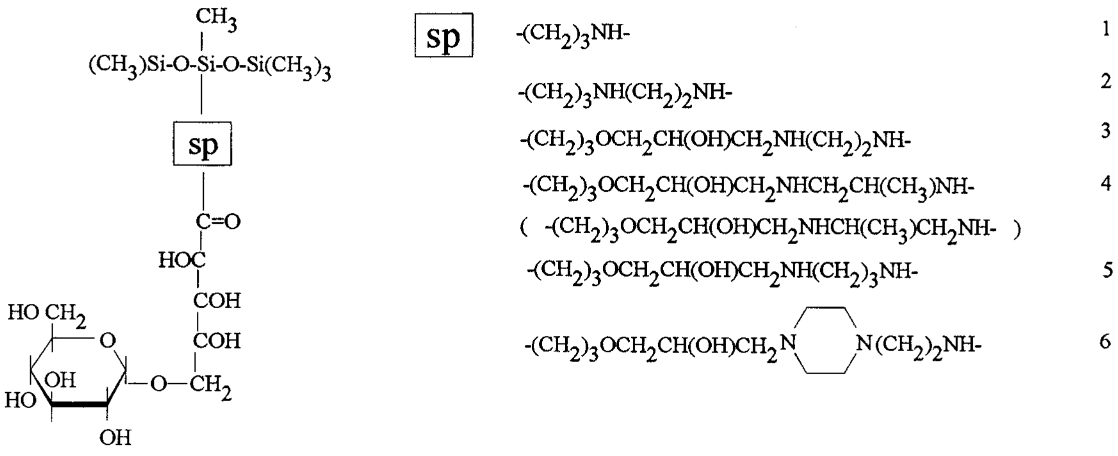


Figure 2 Spacer variations.

3 RESULTS AND DISCUSSION

3.1 Solid surface tension of FEP®

An essential precondition for the accurate determination of the interfacial data of the surfactant adsorption layers is the characterization of the solid surface. Wetting experiments with strictly nonpolar liquids give access to the solid surface tension (γ_{sv}), which is not directly measurable. In Table 1 the results of wetting experiments with different n-alkanes are summarized; according to these data FEP® possesses a solid surface tension of about 18.9 mN m^{-1}. As siloxane surfactants reduce the surface tension of water to 20 mN mN m^{-1}, a spreading of the aqueous surfactant solutions on FEP® is not to be expected. Surfactant structure changes can only effect contact angle differences.

A second important aspect is the practical convergence of the calculated γ_{sv}^{LW} (van Oss[20]) and γ_{sv} (Neumann[21]) data for the lower n-alkanes. The approach of Neumann excludes the existence of a polar interfacial tension contribution, whereas the concept of van Oss is founded on it. Identical results within the error limits mean that a donor–acceptor contribution to the solid surface tension does not exist and the calculated γ_{sl} stems exclusively from Lifshitz–van der Waals interactions. This fact simplifies the calculations for the surfactant adsorption layers. The increasing differences for higher n-alkanes are essentially due to the difference in the treatment, in the course of the formulation of the final equations [6] and [7] , of the important interaction parameter Φ. Van Oss puts Φ = 1 for nonpolar liquids, whereas Neumann[21] introduces a γ_{sl}-dependent Φ (Eqn [11]). For nonpolar liquids possessing surface tensions considerably different from the solid surface tension, the two approaches yield increasingly divergent results.

$$\Phi = -0.0075\ \gamma_{sl} + 1 \qquad [11]$$

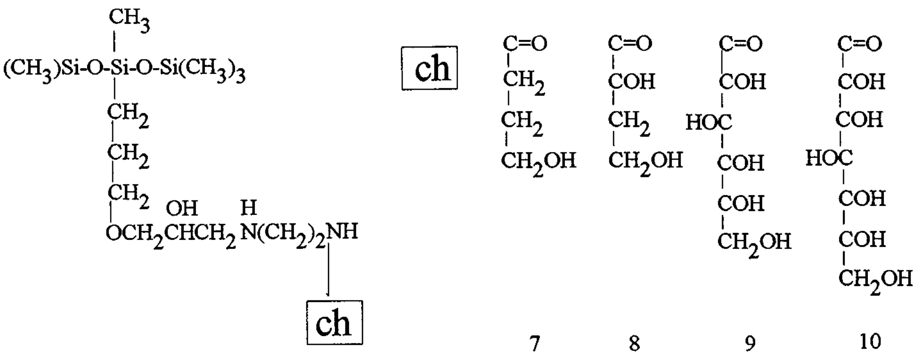


Figure 3 Carbohydrate variations.

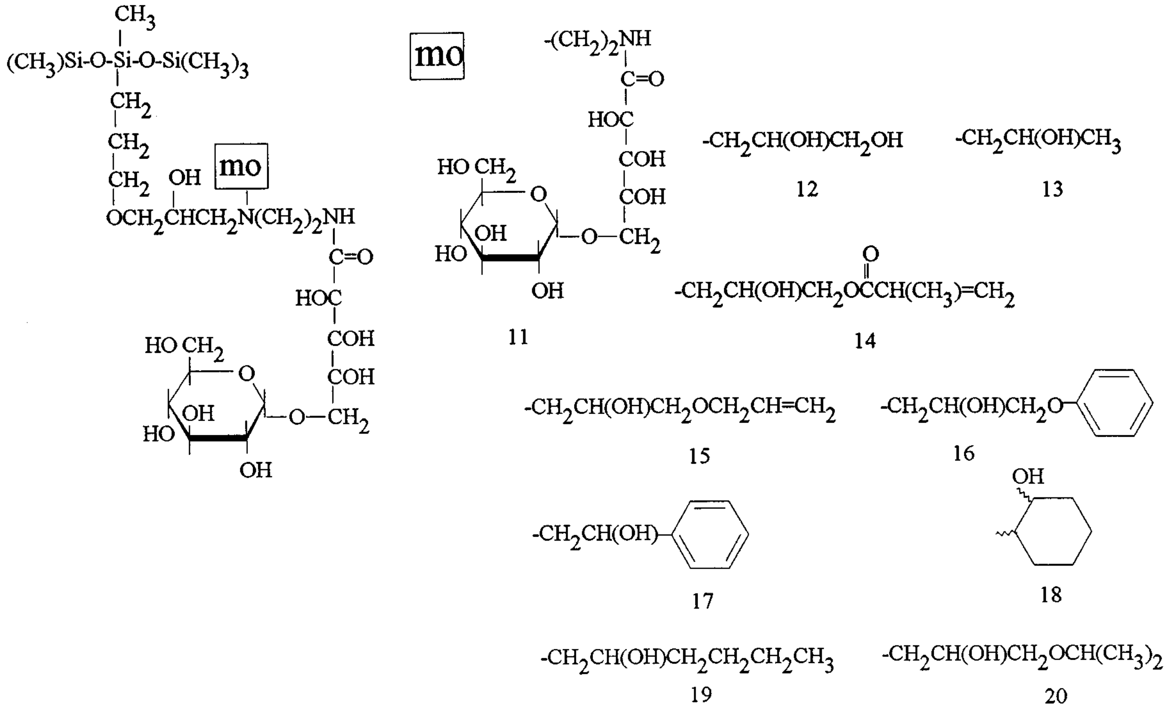


Figure 4 Variations of the modifying element.

3.2 Surface tension, wetting tension, contact angle and spreading behaviour of surfactant solutions

In Tables 2–7 the results of our measurements on aqueous surfactant solutions are summarized.

4 DISCUSSION

4.1 Surface tension (γ_{lv})

The data in Tables 2–6 show that, with few (but important) exceptions, all siloxane surfactants

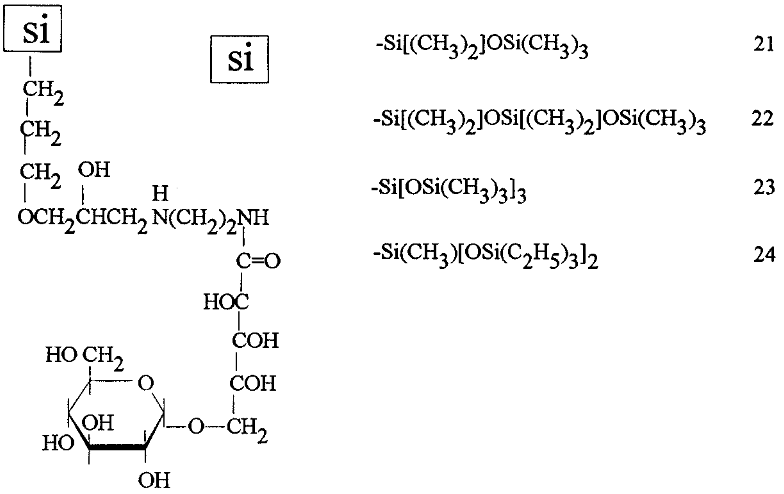
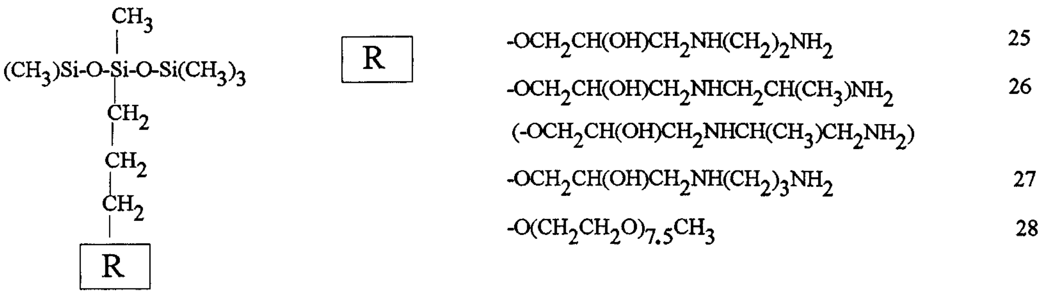


Figure 5 Siloxane variations.



R	
$-OCH_2CH(OH)CH_2NH(CH_2)_2NH_2$	25
$-OCH_2CH(OH)CH_2NHCH_2CH(CH_3)NH_2$ $(-OCH_2CH(OH)CH_2NHCH(CH_3)CH_2NH_2)$	26
$-OCH_2CH(OH)CH_2NH(CH_2)_3NH_2$	27
$-O(CH_2CH_2O)_{7.5}CH_3$	28

Figure 6 Aminosiloxanes.

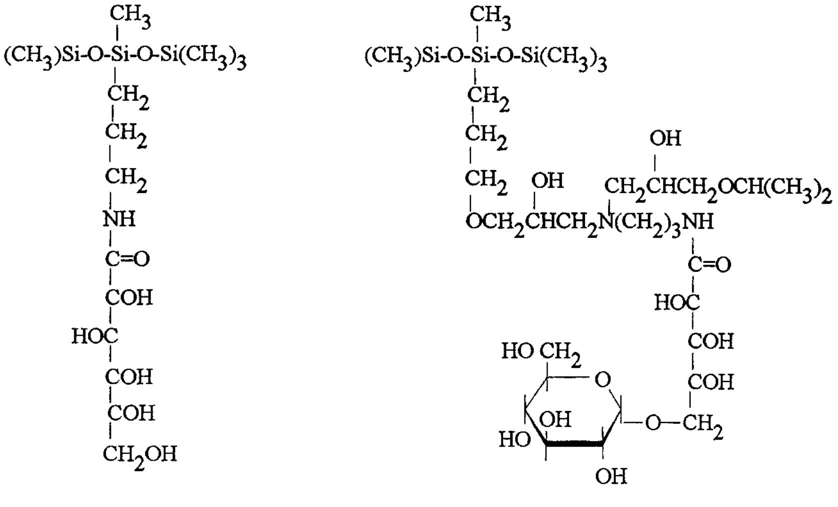
lower the surface tension of water to 20–22 mN m^{-1}.

The siloxanyl moiety possesses an extraordinary capacity to level out impacts of other structural elements. It is important to state that changes in neither the spacer nor carbohydrate structure were found to have any significant influence on this property.

The systematic variation of the modifying element yields a first exception. After incorporation of a second disaccharide unit (Fig. 9, compound **11**) the surface tension rises to 25 mN m^{-1}. Obviously two carbohydrate units are hydrophilic and bulky enough (surface area per carbohydrate ring[25] about 35 Å^2) to hinder the permethylated trisiloxanyl moieties (surface area[26,27] about 50 Å^2) from occupying optimum positions at the liquid/vapour interface. To a much smaller extent aromatic ring systems also seem to be able to increase the surface tension (compound **16**).

Considering the dominant role of the siloxanyl moiety, variations of its structure should effect the most significant changes. In contrast to the findings of Schmaucks,[26] the disiloxanyl (compound **21**) and straight-chained trisiloxanyl (compound **22**) moieties yield almost identical surface tensions, whereas the branched trisiloxane (compound **3**) more effectively lowers the surface tension (Fig. 9). This result becomes reasonable if one considers the analogous behaviour of 'effective' branched and 'efficient' straight-chained hydrocarbon-based surfactants.[28]

As expected, a deviation (compound **24**) from the successful 'permethylated Si–O–Si backbone' structure concept yields a drastic effect. The accumulation of bulkier ethyl groups reduces to a certain extent the chain flexibility. The additional presence of higher-energy $-CH_2-$



29 30

Figure 7 Other siloxane surfactants investigated.

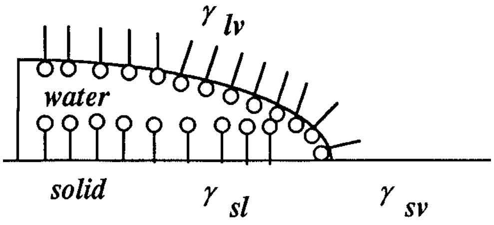


Figure 8 A drop of surfactant solution on a nonpolar solid.

groups [29] (compared with –CH_3 groups) also provides a contribution to the increased surface tension.

Although a detailed analysis of the structure–surface tension dependence provides some interesting information concerning the role of certain substructures in siloxane surfactants, conclusive approaches for the understanding of the sometimes intriguing wetting phenomena on nonpolar and low-energy solid surfaces are not generated. Additional parameters have to be considered.

4.2 Contact angle (θ)

Although the contact angle of a liquid on a given solid material (constant solid/vapour interfacial tension γ_{sv}) by definition (Young equation, Eqn [4]) depends on the surface tension and the solid/liquid interfacial tension, there is a widespread opinion that low surface tensions effect low contact angles and vice versa, high surface tensions yield higher contact angles. This idea of a strictly surface tension-dependent contact angle finds is manifestation in Neumanns[21] ‘equation

Table 1 Wetting of FEP® by n-alkanes

n-Alkane	γ_{lv} (mN m^{-1})	α (mN m^{-1})	cos Θ	γ_{sv}^{LW} (mN m^{-1}) (van Oss)	γ_{sv} (mN m^{-1}) (Neumann)	$\lvert\gamma_{sv}^{LW} - \gamma_{sv}\rvert$ (mN m^{-1})
Heptane	20.7	19.2	0.9272	19.2	19.2	0
Octane	21.9	18.3	0.8387	18.5	18.5	0
Nonane	23.4	18.8	0.7986	19.0	19.1	0.1
Decane	23.8	18.6	0.7771	18.9	19.0	0.1
Dodecane	25.6	18.5	0.7193	19.0	19.2	0.2
Tetradecane	25.9	18.1	0.6820	18.6	18.9	0.3
Hexadecane	28.5	18.0	0.6293	18.9	19.3	0.4

Table 2 Dependence of the interfacial properties on the spacer structure (sp)

Compd	cmc (mol l^{-1})	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})	γ_{sl} (mN $m^{-1]}$)	γ_{sl}^{LW} (mN m^{-1})	α (mN m^{-1})	Θ (deg)	Ω_F ($Å^2$ mol^{-1}	$\Delta G^{\ominus}$ (kJ mol^{-1})
1	8.0×10^{-4}	21.1	19.5	1.6	2.0	0.01	16.9	36	43	−8.1
2	1.3×10^{-3}	21.5	19.8	1.9	1.7	0.01	27.2	37	31	−3.9
3	7.5×10^{-4}	21.5	19.0	2.5	2.4	0	16.5	40	52	−9.7
4	4.1×10^{-4}	20.7	19.7	1.0	1.0	0.01	17.9	30	43	−8.1
5	7.5×10^{-4}	20.8	19.7	1.1	1.1	0.01	17.8	31	37	−5.6
6	8.0×10^{-4}	21.6	19.7	1.9	1.8	0.01	17.1	38	37	−7.2

Table 3 Dependence of the interfacial properties on the carbohydrate structure (ch)

Compd	cmc (mol l^{-1})	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})	γ_{sl} (mN $m^{-1]}$)	γ_{sl}^{LW} (mN m^{-1})	α (mN m^{-1})	Θ (deg)	Ω_F ($Å^2$ mol^{-1}	$\Delta G^{\ominus}$ (kJ mol^{-1})
7	1.0×10^{-4}	21.2	19.9	1.3	1.3	0.01	17.6	34	41	−8.4
8	6.0×10^{-4}	21.3	20.1	1.2	1.2	0.02	17.7	34	42	−8.0
9	1.4×10^{-3}	21.0	19.8	1.2	1.2	0.01	17.7	32	49	−5.9
10	5.9×10^{-4}	21.3	20.1	1.2	1.2	0.02	17.7	34	39	−5.6

Table 4 Dependence on the interfacial properties on the modifying element structure (mo)

Compd	cmc (mol l^{-1})	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})	γ_{sl} (mN m^{-1l})	γ_{sl}^{LW} (mN m^{-1})	α (mN m^{-1})	Θ (deg)	Ω_F (Å^2 mol^{-1}	$\Delta G^{\ominus}$ (kJ mol^{-1})
11	2.9×10^{-4}	25.0	20.6	4.4	4.4	0.04	14.5	55	51	−12.7
12	2.3×10^{-4}	20.7	18.9	1.8	1.8	0	17.1	34	43	−9.0
13	9.5×10^{-5}	21.0	19.6	1.4	1.4	0.01	17.5	34	27	−8.4
14	8.0×10^{-5}	20.9	20.6	0.3	0.3	0.04	18.6	27	40	−9.6
15	1.0×10^{-4}	21.2	19.9	1.2	1.3	0.01	17.6	34	32	−6.6
16	9.0×10^{-5}	22.2	20.2	2.0	1.7	0.02	17.2	40	35	−6.7
17	5.6×10^{-5}	21.8	20.2	1.6	1.6	0.02	17.3	38	37	−6.0
18	—	22.2	20.4	1.8	1.8	0.03	17.1	40	—	—
19	—	21.0	20.1	0.9	0.9	0.02	18.0	31	—	—
20	1.2×10^{-4}	20.9	20.4	0.5	0.5	0.03	18.4	28	41	−8.3

of state' approach (Eqn. [7]).

However, it neglects the chemists daily experience that interactions and reactions between two different molecules often depend decisively on polarized substructures of both partners. If this is true, the result of a surface tension measurement (the interaction partner of the liquid is the 'diluted material', air) cannot describe the interaction situation at the solid/liquid interface (the interaction partner is a condensed and more or less polar material).

Surfactant solutions represent a special case. Here the homogeneous liquid is replaced by a 'core–shell system' consisting of water as core phase and a surfactant monolayer as shell. Due to the polarity of the water and the ambivalent character of the surfactant (chemically connected but separated extreme polar and nonpolar moie-

Table 5 Dependence of the interfacial properties on the siloxane structure (si)

Compd	cmc (mol l^{-1})	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})	γ_{sl} (mN m^{-1l})	γ_{sl}^{LW} (mN m^{-1})	α (mN m^{-1})	Θ (deg)	Ω_F (Å^2 mol^{-1}	$\Delta G^{\ominus}$ (kJ mol^{-1})
21	6.4×10^{-4}	21.9	20.7	1.2	1.2	0.04	17.7	36	35	−2.0
22	4.4×10^{-4}	22.2	21.0	1.2	1.2	0.06	17.7	37	35	−0.5
23	2.8×10^{-4}	22.6	20.4	2.2	2.2	0.03	16.7	42	38	−4.8
24	4.0×10^{-4}	26.9	25.5	1.4	1.9	0.49	17.0	51	47	−5.4

Table 6 Interfacial properties of aminosiloxanes and Silwet L-77

Compd	cmc (mol l^{-1})	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})	γ_{sl} (mN m^{-1l})	γ_{sl}^{LW} (mN m^{-1})	α (mN m^{-1})	Θ (deg)	Ω_F (Å^2 mol^{-1}	$\Delta G^{\ominus}$ (kJ mol^{-1})
25	1.8×10^{-5}	20.4	19.2	1.2	1.2	0	17.7	30	33	−13.5
26	—	20.6	19.4	1.2	1.2	0.01	17.7	31	—	—
27	—	20.3	19.5	0.8	0.8	0.01	18.1	27	—	—
28	1.7×10^{-4}	20.9	19.5	1.4	1.4	0.01	17.5	33	49	—
28 bulk	—	24.6	20.8	3.8	2.7	0.05	15.1	52	—	—

Table 7 Spreading of dilute surfactant solutions on polypropylene (50 μl drop volume, 0.1% by wt aqueous solutions, 20 °C, 70% relative humidity)

Compd	**3**	**4**	**5**	**7**	**9**	**25**	**26**	**27**	**28**	**28** (1%)	**29**	**30**
Area (cm^2)	2.5	7.1	3.8	38.4	9.6	33.1	56.7	28.2	50.2	11.3	30.1	15.1

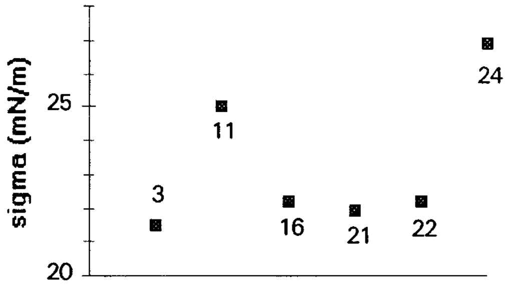


Figure 9 Surface tensions of aqueous solutions of selected siloxane surfactants.

ties), highly oriented surfactant monolayers are formed. Nevertheless, if (1) both interfaces are almost exclusively covered by surfactant molecules, (2) both monolayers are in a stable long-term equilibrium and (3) the monolayers are sufficiently thick to determine the interfacial properties, one can expect conclusive results concerning the correlation between surfactant structure and wetting properties.

Of course, results identical to those obtained for pure liquids cannot be expected (the extremely different data sets for compound **28** in bulk and in solution immediately emphasize this consideration; Table 6).

Yaminsky[30] investigated the adsorption of cetyltrimethylammonium bromide (CTAB) solutions on silica glass by wetting tension measurements. Due to the polar nature of the substrate at low surfactant concentrations, the solid/vapour interface is covered preferentially. At higher concentrations a surfactant double layer at the solid/liquid interface is formed.

Lunkenheimer[31] found increasing contact angles on different PTFE samples after treatment with solutions of a cationic surfactant. He concluded that sulphate groups on the PTFE surface (incorporated by the polymerization initiator peroxodisulphate; no PTFE sample was found to be completely nonpolar) are neutralized by the quaternary ammonium groups of the cationic surfactant, yielding an additional hydrophobization of the perfluorinated material.

Wolfram[32] systematically investigated the concentration dependence of contact angle and wetting tension for sodium dodecylsulphate solutions on PTFE. According to his results the contact angle decreases with increasing concentration whereas the wetting tension increases. It is important to note that, at concentrations above the cmc, contact angle and wetting tension values are constant.

The latter phenomenon was used by Richter[19] to analyse the wetting behaviour of solutions of alkyl and alkylaryl oxethylates on an FEP® plate. He found that the contact angle above the cmc (calculated from surface tension, wetting tension and a known, constant, solid surface tension) and the polar portion of the surface tension, increase with the number of ethylene oxide units. The dispersion portion of the surface tension remained constant. Although only a few surfactants had been analysed, these results indicate that in homologous series the relevant interfacial parameters are a function of the chemical structure of the surfactant.

Analysis of the contact angle data for the siloxane surfactants provides an apparently confusing picture. In the majority of cases, surfactant solutions with high surface tensions also yield high contact angles (Fig. 10; compounds **14** and **20** → **16** and **17**).

Nevertheless, systematic derivatizations have made surfactant pairs accessible where constant or increasing surface tensions are accompanied by decreasing contact angles. Thus the substitution of a dihydroxylated compound (**12**) by methylated modifying elements (compounds **14** and **20**) yields significantly lower contact angles despite slightly increased surface tensions.

Derivatizations of the siloxanyl substructure cause the most interesting effects. An instructive case represents a pair of isomeric branched (**22**) and straight-chained (**3**) trisiloxanyl compounds. Although the branched trisiloxane more effectively reduces the surface tension, a higher contact angle is found (Fig. 10). The reason for this behaviour becomes clear if one considers the data sets for the substances with the highest surface tensions. In compound **24** six (hydrophobic) ethyl groups cause the high surface

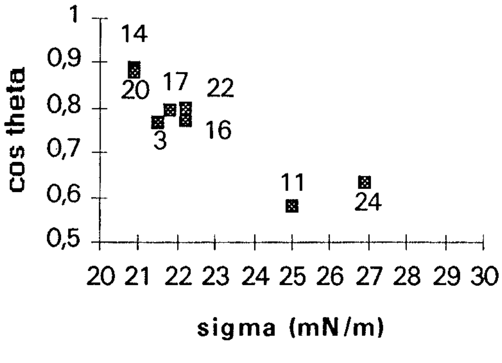


Figure 10 Surface tensions and contact angles of aqueous solutions of selected surfactants.

tension (26.9 mN m^{-1}), whereas in substance **11** two (hydrophilic) carbohydrate units increase the surface tension to 25.0 mN m^{-1} the latter surfactant shows a poorer wetting behaviour (Fig. 10).

Obviously, perfluorinated nonpolar solid materials can interact selectively with surfactants, generating predominantly Lifshitz–van der Waals forces (a moderate increase of the contact angle for compound **24** is found), whereas increased donor–acceptor portions remain uncompensated and cause a much stronger contact angle increase (compound **11**).

Considering the Young equation, this behaviour has to be due to an independent interfacial tension γ_{sl}.

4.3 Solid/liquid interfacial tension (γ_{sl})

If the solid/liquid interfacial tension is not strictly dependent on the surface tension γ_{lv}, reasonable correlations between chemical structure and solid/liquid interfacial tension have to exist.

First it is noteworthy that additional methyl groups decrease γ_{sl}. The low contact angles of compounds **14** and **20** compared with the hydroxylated compound (**12**) are therefore due to lower γ_{sl} values (Fig. 11).

Aqueous solutions of compounds **2** and **3** have the same surface tension. Additional polar substructures (compound **3**, –O–, –OH) yield an increased γ_{sl} and contact angle value.

A renewed comparison of the isomeric straight-chained **22** and branched **3** trisiloxanyl derivatives is very instructive for the understanding of the interactions at the nonpolar solid/liquid interface. The lower contact angle of the straight-chained isomer (**22**) is due to a drastically reduced γ_{sl} value which overrules the higher surface tension (Fig. 11). On a molecular level this situation is illustrated in Fig. 12.

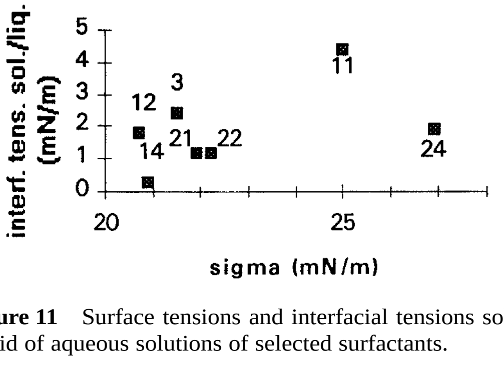


Figure 11 Surface tensions and interfacial tensions solid/liquid of aqueous solutions of selected surfactants.

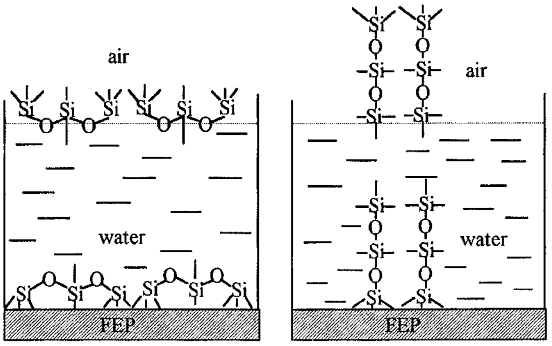


Figure 12 Orientation of branched (left) and straight-chained (right) siloxanyl units at interfaces.

Due to the absence of a condensed partner (air is too dilute) the interactions of hydrophobic parts of surfactant molecules at the liquid/vapour interface have to be laterally oriented. Therefore straight-chained structures (with higher orientation) usually yield higher surface tensions than branched ones.[28] At the solid/liquid interface the condensed partner (which in our case is nonpolar) substantially influences the interaction behaviour of the hydrophobic part of the molecule. The lateral interactions between the surfactants' hydrophobic moieties are superposed by interactions between the solid and the surfactants' hydrophobic moieties.

Methyl groups of siloxanyl structures are bulky enough to prevent a direct exposure of oxygen atoms to the perfluorinated surface.[29] But they cannot suppress a certain depth influence of the oxygen atoms. If one considers both (1) the differences in the specific area per molecule [(with similar packing at both interfaces,[33] at the liquid/vapour interface 40 Å^2 (**22**)[26] and 50 Å^2 (**3**)[26,27]] and (2) in (**22**) the significantly greater distance to the solid surface of the second oxygen atom (Fig. 12, right-hand diagram), an effective reduction of the polarity for **22** can be assumed. It is the opinion of the authors that in this particular case the reduced polarity is the reason for the lower γ_{sl} and θ values.

Again, an analysis of the data of the two surfactants which yielded unusually high surface tensions (compounds **11** and **24**) supports this view (Fig. 11). Substance **11** is highly polar and the two independent and bulky carbohydrate substructures per siloxanyl moiety hinder the hydrophobic unit from occupying an optimum (low-energy) position at the liquid/vapour interface. The same can be assumed at the solid/liquid interface as this geometric argument does not change. Consequently, in analogy to γ_{lv}, the value of γ_{sl} increases considerably. (On the basis of the data available we cannot decide conclusively on the origin of the increased γ_{sl}. Do parts of the polar carbohydrate rings simply 'look through' to the solid surface, or are surfactant molecules—under the impact of the powerful carbohydrate units—already desorbed to such an extent that minor portions of polar water have to fill the gaps?)

As expected from the discussion of the contact angle data, the hexaethyl-substituted compound **24** shows a different behaviour. Due to possible selective interactions of the Lifshitz–van der Waals type, the high surface tension is not accompanied by an increased γ_{sl}.

The results presented above clearly demonstrate that increased donor–acceptor as well as Lifshitz–van der Waals interactions increase the surface tensions of aqueous surfactant solutions. On the other hand increasing donor–acceptor interactions also raise the solid/liquid interfacial tension considerably. Stronger nonpolar Lifshitz–van der Waals interactions influence γ_{sl} to a much lower extent at the interface with a nonpolar solid.The point that in only a few cases do these effects clearly become visible once more emphasizes the enormous capacity of siloxanyl moieties to level out the interfacial properties.

4.4 Donor–acceptor ($\gamma^{+/-}$) and Lifshitz–van der Waals (γ^{LW}) portions of the surface tension and solid/liquid interfacial tension

The explanation for the existence of an independent solid/liquid interfacial tension (see Section 4.3 above) is founded on considerations concerning increased or decreased donor–acceptor and Lifshitz–van der Waals interactions. A quantification of these terms should help to improve the understanding of the power balance at the interfaces.

Neumann's[34] 'equation of state' approach (Eqn [12]) for a surface tension-dependent γ_{sl} by definition does not provide answers on this question.

$$\gamma_{sl} = \frac{(\sqrt{\gamma_{sv}} - \sqrt{\gamma_{lv}})^2}{1 - 0.015\sqrt{\gamma_{sv} \cdot \gamma_{lv}}} \qquad [12]$$

By treating the three interfacial tensions as independent and consisting of donor–acceptor (+/−) and Lifshitz–van der Waals (LW) contributions, Good and co-workers[20] developed a system based on selective interactions (Eqn [13]):

$$\gamma_{sl} = (\sqrt{\gamma_{sv}^{LW}} - \sqrt{\gamma_{lv}^{LW}})^2 + 2(\sqrt{\gamma_{sv}^{+} \cdot \gamma_{sv}^{-}} + \sqrt{\gamma_{lv}^{+} \cdot \gamma_{lv}^{-}} - \sqrt{\gamma_{sv}^{+} \cdot \gamma_{lv}^{-}} - \sqrt{\gamma_{sv}^{-} \cdot \gamma_{lv}^{+}}) \qquad [13]$$

Although this approach for a selective treatment of donor–acceptor and Lifshitz–van der Waals contributions is in line with chemists' experience of selective mutual attractions during the course of nucleophilic/electrophilic reactions, the quantification of these interactions on the present level of understanding seems to be not completely satisfactory. In a number of cases major deviations of the experimental results from theoretical predictions have been found.[35]

Therefore the authors are aware that the donor–acceptor and Lifshitz–van der Waals portions of the surface tension and solid/liquid interfacial tension do not entirely describe the absolute polarity of a single molecule. Instead they reflect its measurable interactions with other surfactant molecules or condensed phases. Data sets for single substances obtain their relevance from comparisons with sets of structurally related compounds.

With few exceptions, the Lifshitz–van der Waals portion of the surface tension (γ_{lv}^{LW}) amounts to 19–20 mN m^{-1} and the donor–acceptor portion ($\gamma_{lv}^{+/-}$) 1–2 mN m^{-1}; this is in good agreement with Owens data[29] for cross-linked polydimethylsiloxanes (19 mN m^{-1} and 1.2 mN m^{-1}). For alkyl chain-substituted trisiloxanes a polar portion of 1.2 mN m^{-1} was determined by Richter.[27] These almost constant values for surfactant monolayers, polymeric surfaces and liquid siloxanes emphasize the role of the methyl group-embedded oxygen atoms at interfaces.

A closer inspection offers additional deviations from that rule, well founded on structural factors.

Although, for a wide range of graded polar carbohydrate structures, practically constant data sets were found (compounds **7**–**10**), the most bulky and hydrophilic carbohydrate units cause a considerably increased donor–acceptor portion whereas the Lifshitz–van der Waals portion remains constant (compound **3**) or is only slightly increased (compound **11**) (Fig. 13).

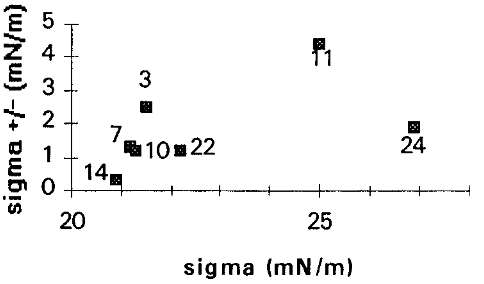


Figure 13 Surface tensions and donor–acceptor portions of aqueous solutions of selected surfactants.

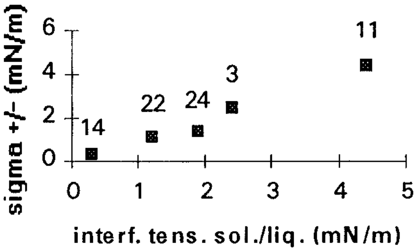


Figure 14 Solid/liquid interfacial tension and the donor–acceptor portion of the surface tension of aqueous solutions of selected surfactants.

The incorporation of additional methyl groups (compounds **4**, **14**, **20**) yields increased Lifshitz–van der Waals portions at the expense of the donor–acceptor portions.

The structure of the siloxane has an important influence on this balance. Structures in which both oxygen atoms are better insulated (compounds **3**→**24**), or where at least one oxygen atom of the siloxanyl moiety is more distant (compounds **3**→**22**) from the water surface, yield a lower donor–acceptor portion. The Lifshitz–van der Waals portions increase considerably.

For the n-octane/oxethylated lauryl alcohol system Becher[33] found that $\gamma_{lv}^{+/-}$ quite closely follows γ_{sl}. The $\gamma_{lv}^{+/-}$ values were somewhat smaller; especially for longer ethylene oxide (EO) chains deviations up to 1 mN m^{-1} appeared. Richter[19] investigated the FEP plate/ethoxylated long-chained alcohols system and found the same dependencies.

Despite the deviations stated, and the fact that nonidentical values for the solid surface tension of nonpolar solids and the Lifshitz–van der Waals contribution to surfactant surface tension yield an interfacial tension contribution (see Eqn [13]), Becher[33] assumed that γ_{sl} almost exclusively stems from the polar contribution of the EO chains in the water phase.

The main difference between our system and those of Becher and Richter is the practical identity of FEP's Lifshitz–van der Waals-based solid surface tension (18.9 mN m^{-1}) and γ_{lv}^{LW} of the siloxane surfactants (19–20 mN m^{-1}). For this principal reason, a Lifshitz–van der Waals contribution γ_{sl}^{LW} is unlikely and $\gamma_{sl}^{+/-}$ (as well as $\gamma_{lv}^{+/-}$) should follow γ_{sl} closely.

It is one of the most exciting aspects of our investigations that despite the tremendous chemical differences and even the structure-dependent $\gamma_{lv}^{+/-}$ values already discussed, this rule is obeyed. For almost every siloxane surfactant, $\gamma_{lv}^{+/-}$ is identical to the independently determined γ_{sl} within the limits of error.

Interestingly, the only serious exception was noticed in the case of the hexaethyl-substituted derivative **24**. Here a considerable difference between strictly apolar solid surface tension and γ_{lv}^{LW} of the surfactant has to be taken into account. A small but significant Lifshitz–van der Waals contribution γ_{sl}^{LW} could emerge. The calculations confirm this consideration. For compound **24** a significant γ_{sl}^{LW} portion was found (Fig. 14).

The convergence of $\gamma_{lv}^{+/-}$, $\gamma_{sl}^{+/-}$ and γ_{sl} in the other cases supports the assumption that donor–acceptor interactions of the same origin and size (caused by the siloxanyl moiety's oxygen atoms and in certain cases by bulky carbohydrates) act on the liquid/vapour and solid/liquid interfaces.

4.5 Spreading of surfactant solutions on polypropylene

In the previous sections we have shown that aqueous siloxane surfactant solutions form monolayers at the liquid/vapour and solid/liquid interfaces stable enough to be investigated by wetting experiments. These measurements had been carried out with an FEP® plate because for energy reasons no aqueous siloxane surfactant solution can spread on that extremely low-energy surface. The regularly appearing contact angles were used as measures to understand the impacts of systematic structure changes on the spreading behaviour on slightly higher-energy surfaces.

Such surfaces of industrial interest have already been investigated. Zhu *et al.*[7] investigated a nonpolar parafilm surface, whereas Tiberg and Cazabat[8,9] tested silylated silicon wafer. From an energy point of view, the latter surface has the disadvantage that a complicating donor–acceptor contribution to γ_{sv} exists. For that reason we decided to carry out the experiments on a strictly nonpolar polypropylene surface.

The results (Table 7) confirm the general trends already outlined for the contact angle and γ_{sl} data. Bulkier and more polar carbohydrate units (compounds **25**→ **7** → **29** → **3**) reduce the ability to spread. The incorporation of hydrophilic spacer elements also decreases the spreading area (compounds **29** → **9**).

This effect can be counterbalanced by additional branching methyl groups.[36] The measured reduction of the contact angle and γ_{sl} is reflected by increased spreading areas, and it is important to note that this general improvement is not influenced by other other structural factors. We found the same tendency for spacer attached methyl groups in poor spreaders with bulky and polar carbohydrate units (compounds **3** → **4**) and weak polar and carbohydrate-free precursors (compounds **25** → **26**) as well as for the methyl groups of a separate modifying element (compounds **3** → **30**).

In the light of these results, polyhydroxylated siloxane surfactants do not represent an alternative to the well-established oxyalkylated types (compound **28**) for the rapid wetting of nonpolar low-energy surfaces. Their natural field of application is at the opposite end of the surface spectrum: highly polar and hydrogen-bonding-susceptible organic and inorganic substrates.

Nevertheless the systematic structural variations and physicochemical characterizations have yielded, in compound **26**, an excellent superspreader. Its activity is mainly due to the presence of the additional methyl group[36] (often also used for end-cappings,[7] as in compound **28**). The fact that the excellent spreading performance of substance **28** in aqueous solution is accompanied by a rather inconspicuous energy data set emphasizes the necessity also to consider the dynamic behaviour and the bulk properties.[1,37] The completely different data for the pure liquid (bulk **28**) explains Zhu's[7] observation that it did not spread on parafilm. In such a case the intramolecular forces (of the donor–acceptor and Lifshitz–van der Waals type) between surface and bulk molecules of substance **28** are too strong to allow a rapid spreading.

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