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Silicon-Modified Carbohydrate Surfactants VII: Impact of Different Silicon Substructures on the Wetting Behaviour of Carbohydrate Surfactants on Low-Energy Surfaces — Distance Decay of Donor–Acceptor Forces

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The wetting behaviour of carbohydrate surfactants bearing siloxane, carbosilane, polysilane or silane moieties has been investigated. By static surface tension (γ_{lv}, σ) and wetting tension ($\gamma_{sv}-\gamma_{sl}$, α) measurements on a non-polar perfluorinated surface (FEP®), the contact angles of aqueous surfactant solutions above the critical micelle formation concentration (cmc) were determined. Surface tension and wetting tension react independently on defined changes in the chemical structure of the surfactant molecules. Siloxane surfactants reduce the surface tension most effectively, whereas for a neopentyl-substituted silane derivative the lowest solid/liquid interfacial tension was found. The data for isomeric siloxanes, carbosilanes and silanes suggest that donor–acceptor forces at solid interfaces have a maximum range of about 4.5 Å. © 1998 John Wiley & Sons, Ltd.

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1 INTRODUCTION

The exceptional property of aqueous solutions of certain trisiloxane surfactants is their ability to wet rapidly low-energy surfaces[1] (e.g. polyethylene, polypropylene, layers of natural waxes). Unfortunately commercially available products (e.g. Silwet L77; Union Carbide) usually consist of complex mixtures bearing species with four to ten ethylene oxide units attached to the trisiloxane moiety.

In spite of this complicating factor, chemical, geometrical, kinetic and energetic influences have been found to govern the superspreading process.[1–5] Nevertheless, clear-cut quantification of the kinetic and energetic situation during the spreading process is still an unsolved and challenging task. Dynamic surface-tension and dynamic interfacial-tension measurements (aqueous surfactant solution versus n-alkanes) suggest that bulk diffusion coefficients of superspreaders are one order of magnitude higher than those of conventional surfactants.[6] Unfortunately such experiments do not simulate the real situation in the system comprising vapour/aqueous surfactant solution/insoluble solid material. A promising alternative could arise from Chaudhury's dynamic experiments[7] on the adsorption of surfactants to a PDMS sheet/PDMS half-sphere system.

In preceding papers[8–10] we described the synthesis of non-ionic siloxanyl-modified carbohydrate surfactants. Due to their strictly defined structure, we were able to quantify the impact of their substructures on the equilibrium wetting behaviour of aqueous surfactant solutions on perfluorinated

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Table 1 ^{13}C-NMR shifts (ppm) of compound **8**

$(\mathit{C}\mathrm{H}_3)_3\mathrm{C}$-	$(\mathrm{CH}_3)_3\mathit{C}$-	$-\mathrm{CH}_2-$	$-\mathrm{CH}_2\mathrm{Si}[(\mathit{C}\mathrm{H}_3)_2]\mathrm{O}-$	$-\mathrm{OSi}[(\mathit{C}\mathrm{H}_3)_2]-$
32.66	30.14	34.76	2.87	0.32

Table 2 Elemental analysis data (%) of compound **8**

C (calcd.)	C (found)	H (calcd.)	H (found)	N (calcd.)	N (found)
48.81	47.64	8.78	8.80	4.07	4.17

solid surfaces.[11] An important conclusion was that to a large extent the siloxane moiety determines the wetting behaviour.

Therefore we started a comprehensive investigation of the impact of different silicon-containing hydrophobes (siloxanes, carbosilanes, polysilanes, silanes) on the wetting process. The wetting behaviour of SiH-functionalized precursors[12] and a broad variety of epoxy derivatives[13] has already been analyzed. It could be shown that surface tension and solid/liquid interfacial tension develop independently. Further, the [Lifshitz–van der Waals contribution]/[donor-acceptor contribution] ratios of both interfacial energies were found to be clear functions of the chemical structure. In the latter paper we also described the syntheses of defined carbohydrate surfactants bearing siloxane, carbosilane, polysilane and silane moieties.

It is the objective of this paper to systematize the impact of various silicon-containing hydrophobes attached to strictly defined carbohydrate hydrophiles on the energetic balance at the liquid/vapour and solid/liquid interfaces in aqueous solution. It is another objective to discuss the range of the different force types occurring at the interfaces and the consequences for the wetting behaviour.

2 MATERIALS AND METHODS

2.1 Materials

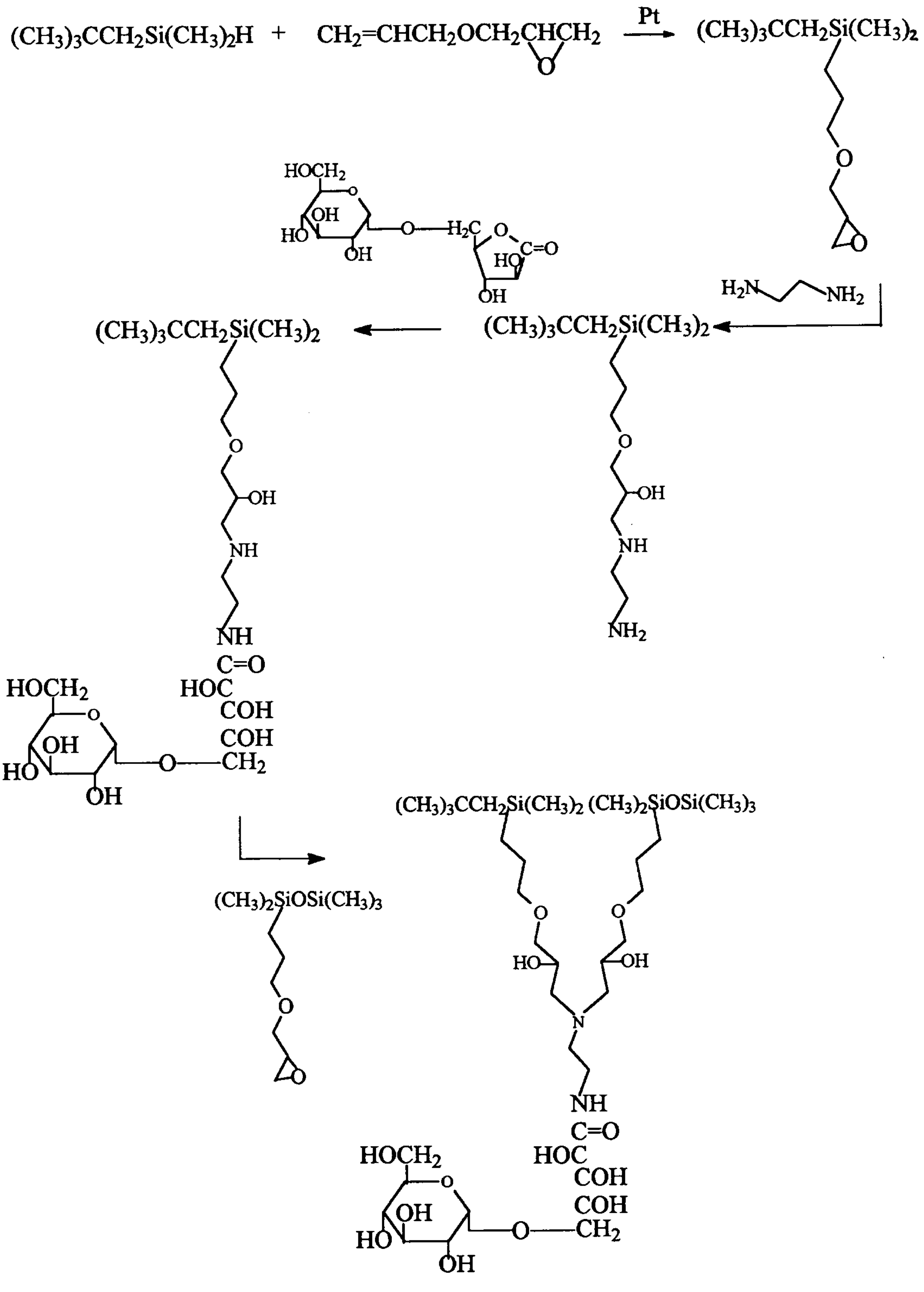
The synthesis and chemical characterization of various silicon-modified carbohydrate surfactants (**1–7** and **9–22**) have been described in earlier papers.[8,9,13] (In view of the complexity of their structure, we use the same numeration for these previously synthesized materials as were given in the original publications.) The neopentyl-substituted disiloxane surfactant **8** was synthesized from the corresponding SiH-functionalized precursor (Scheme 1) via the allyl glycidyl derivative. Table 1 and Table 2 summarize the analytical data for compound **8**.

Scheme 2 demonstrates the general synthetic concept yielding carbohydrate derivatives from SiH-functionalized precursors.

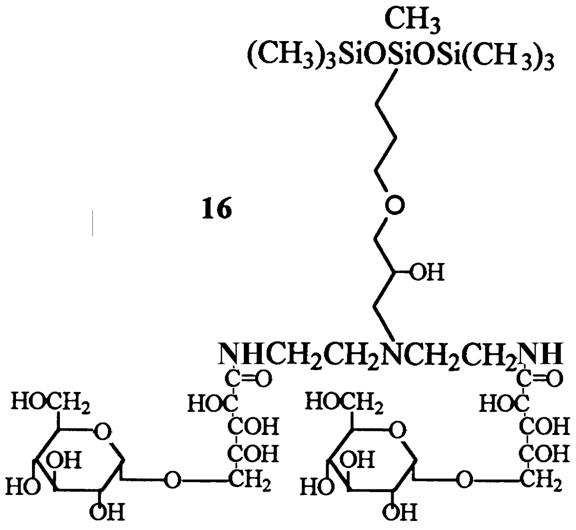
$$(\mathrm{CH}_3)_3\mathrm{CCH}_2\mathrm{MgCl} + (\mathrm{CH}_3)_2\mathrm{SiCl}_2 \xrightarrow{\mathrm{THF}} \underset{\text{B.p. } 144\,^{\circ}\mathrm{C}}{(\mathrm{CH}_3)_3\mathrm{CCH}_2\mathrm{Si}(\mathrm{CH}_3)_2\mathrm{Cl}}$$

$$\underset{\underset{[\mathbf{8}]}{\text{B.p. } 57-60\,^{\circ}\mathrm{C}/30\ \mathrm{mmHg}}}{(\mathrm{CH}_3)_3\mathrm{CCH}_2\mathrm{Si}[(\mathrm{CH}_3)_2]\mathrm{OSi}[(\mathrm{CH}_3)_2]\mathrm{H}} \xleftarrow[\text{dioxane/H}_2\text{SO}_4\ (10\%\ \text{aq. soln})]{(\mathrm{CH}_3)_2\mathrm{ClSiH}}$$

Scheme 1


(CH3)3CCH2Si(CH3)2H + CH2=CHCH2OCH2CHCH2
Pt
(CH3)3CCH2Si(CH3)2
O
HOCH2
OH
HO
OH
O—H2C
C=O
HO
OH
H2N
NH2
(CH3)3CCH2Si(CH3)2
OH
NH
NH2
NH
C=O
HOC
COH
COH
CH2
(CH3)2SiOSi(CH3)3
(CH3)3CCH2Si(CH3)2 (CH3)2SiOSi(CH3)3
HO
N

Scheme 2



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For comparative purposes we also now include the already published[11] data for a branched derivative bearing two disaccharide moieties, compound **16**.

2.2 Methods

The ^{13}C-NMR spectrum of compound **8** was recorded on a Varian XL 300 spectrometer using deuterated DMSO as solvent and internal standard. The elemental analysis data were determined on a Carlo Erba analyser, model 1106.

The macroscopic behaviour of a liquid on a plane solid surface is determined by the equilibrium of three forces: (1) the liquid/vapour interfacial tension (surface tension of the liquid γ_{Lv} or σ; (2) the solid/vapour interfacial tension (solid surface tension γ_{sv}; and (3) the solid/liquid interfacial tension γ_{sL} (Fig. 1). It is expressed by the well-known Young equation[14] (Eqn [1]):

$$\frac{\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}}}{\gamma_{\mathrm{lv}}} = \frac{\alpha}{\sigma} = \cos\theta \qquad [1]$$

where α is the wetting tension and θ is the contact angle.

The contact angles of aqueous surfactant solutions with concentrations above the critical micelle (cmc) concentration ($c > c_{\mathrm{cmc}}$) on non-polar FEP® plates (tetrafluoroethylene–hexafluoropropylene copolymer; Du Pont) were determined according to Eqn [1] by independently measuring surface tension γ_{Lv} (ring method, data corrected according to Harkins and Jordan[15]) and wetting tension α (Wilhelmy method). Each measurement was carried out at 20 °C.

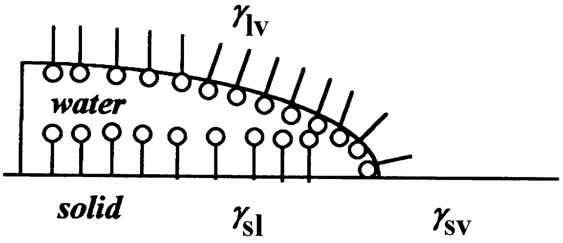


Figure 1 Surfactant solution drop on a non-polar solid.

To measure the wetting tension α, an FEP® plate of defined width and thickness is dipped stepwise (0.2 cm) into the surfactant solution with an accuracy of 0.001 cm. The force (p) measured correlates with α according to Eqn [2]:

$$p = u\alpha + (-)\rho \mathbf{g} d b x_{\mathrm{e}} \qquad [2]$$

where u = perimeter of the FEP® plate, ρ = liquid density, g = gravitational constant, d = thickness of the plate, b = width of the plate and x_{e} = immersion depth of the plate.

After every movement of the plate we measured the force immediately and also after 5 min. This time was found to be necessary for the system to reach an equilibrium state of wetting. A plot of the 5-min values of the force p against the immersion depth x_{e} yields, after extrapolation to x_{e} = O, the wetting tension (α)

The procedure for the determination of the solid surface tension γ_{sv} has been described previously[11]. The value $\gamma_{\mathrm{sv}} = \gamma_{\mathrm{sv}}^{\mathrm{LW}} = 18.9\ \mathrm{mN\ m^{-1}}$ has been used for all calculations.

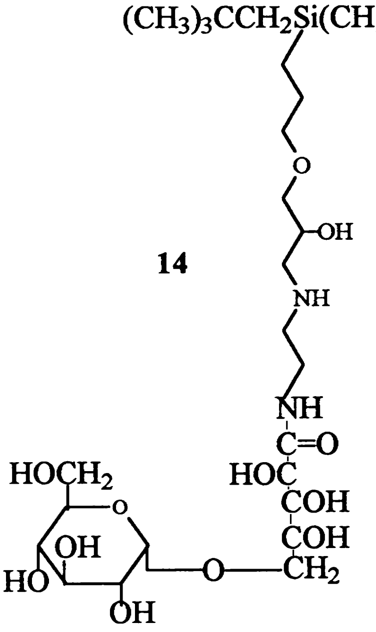
The interfacial tension γ_{sl} was calculated as $\gamma_{\mathrm{sv}} - \alpha$ (see Eqn [1]).

The fact that FEP® is strictly non-polar eliminates a complicating $\gamma_{\mathrm{sv}}^{+/-}$ term from the calculations. Therefore we were able in a simple way to determine the Lifshitz–van der Waals portions of the surface tension[16] (γ_{lv}^{LW}) (Eqn [3]) and solid/liquid interfacial tension[17] ($\gamma_{\mathrm{sl}}{}^{\mathrm{LW}}$) (Eqn [4]):

$$\gamma_{\mathrm{lv}}^{\mathrm{LW}} = \left[\frac{\gamma_{\mathrm{lv}}(1+\cos\theta)}{2\sqrt{\gamma_{\mathrm{sv}}^{\mathrm{LW}}}}\right]^2 \qquad [3]$$

$$\gamma_{\mathrm{sl}}^{\mathrm{LW}} = \gamma_{\mathrm{sv}}^{\mathrm{LW}} + \gamma_{\mathrm{lv}}^{\mathrm{LW}} - 2\sqrt{\gamma_{\mathrm{sv}}^{\mathrm{LW}}\gamma_{\mathrm{lv}}^{\mathrm{LW}}} \qquad [4]$$

The polar portions ($\gamma_{\mathrm{lv}}{}^{+/-}$) and ($\gamma_{\mathrm{sl}}{}^{+/-}$) were



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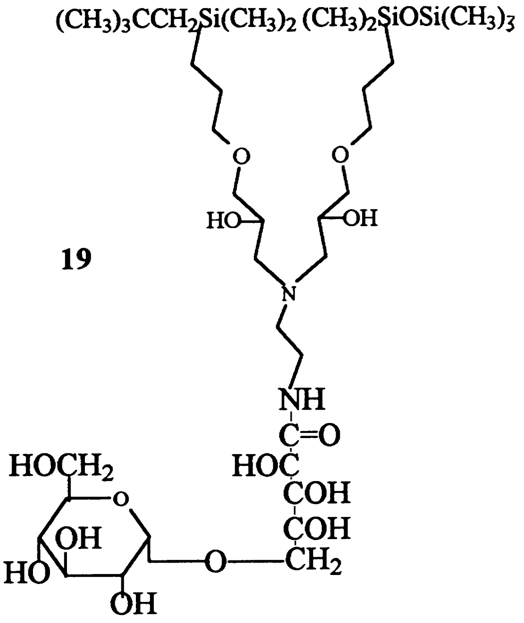

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calculated according to Fowkes' approach[18] (Eqns [5] and [6]):

$$\gamma_{\mathrm{lv}} = \gamma_{\mathrm{lv}}^{\mathrm{LW}} + \gamma_{\mathrm{lv}}^{+/-} \quad [5]$$

$$\gamma_{\mathrm{sl}} = \gamma_{\mathrm{sl}}^{\mathrm{LW}} + \gamma_{\mathrm{sl}}^{+/-} \quad [6]$$

3 RESULTS

3.1 Surface tensions, wetting tensions and contact angles of the surfactant solutions

Table 3 and Table 4 summarize the results of our measurements on aqueous surfactant solutions above the cmc. These tables concern straight-chained surfactants of the type of compound **14** as well as double-chained structures with two independent Silicon-containing hydrophobes (e.g. **19**).

4 DISCUSSION

In an earlier paper[4] we were able to show how the different substructures of strictly defined siloxanyl-modified carbohydrate surfactants (siloxane moiety, spacer, carbohydrate unit, modifying element) influence the equilibrium wetting behaviour on a perfluorinated solid surface. It was demonstrated that a siloxanyl moiety plays an even more dominant role than the hydrocarbon chain in a hydrocarbon-based surfactant. As only few different siloxanyl structures were available, a detailed investigation of this specific phenomenon could not be carried out. The few and incomplete literature data[19–22] do not fill the gap.

Therefore we synthesized[8,9,13] surfactants covering four different features of Silicon-containing hydrophobes:

(1) branched trisiloxanes with substituents other than methyl (compounds **1–4**);
(2) variably substituted disiloxane structures (compounds **5–11**);
(3) polysilanes, carbosilanes, neopentyl-substituted silanes (compounds **12–14**);
(4) double-chained structures (compounds **17–22**).

4.1 Branched trisiloxane structures

The wetting results for aqueous solutions of branched trisiloxane surfactants are in line with the trends already outlined for the corresponding liquid epoxides.[6]

Table 3 Silicon-containing hydrophobes attached to the carbohydrate moiety

(a) Straight-chained Structures

Compd	Silicon moiety	Compd	Silicon moiety
1	$[(CH_3)_3SiO]_2Si(CH_3)$–	**9**	$(CH_3)_3CSi[(CH_3)_2]OSi[(CH_3)_2]$–
2	$[(CH_3)_3SiO]_2Si(C_2H_5)$–	**10**	$(CH_3)_3CCH_2CH_2Si[(CH_3)_2]OSi[(CH_3)_2]$–
3	$[(C_2H_5)_3SiO]_2Si(CH_3)$–	**11**	$(CH_3)_3SiOSi[(CH_3)_2]$–
4	$[(CH_3)_3SiO]_2Si(C_5H_6)$–	**12**	$(CH_3)_3SiSi[(CH_3)_2]$–
5	$(CH_3)_3SiOSi[(CH_3)_2]OSi[(CH_3)_2]$–	**13**	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–
6	$(CH_3)_3SiOSi[(CH_3)_2]CH_2Si[(CH_3)_2]$–	**14**	$(CH_3)_3CCH_2Si[(CH_3)_2]$–
7	$(CH_3)_3SiCH_2Si[(CH_3)_2]OSi[(CH_3)_2]$–	**15**	$(CH_3)_3Si$–
8	$(CH_3)_3CCH_2Si[(CH_3)_2]OSi[(CH_3)_2]$–		

(b) Double-chained structures

Compd	Silicon moiety 1	Silicon moiety 2
17	$(CH_3)_3SiOSi[(CH_3)_2]$–	$(CH_3)_3SiOSi[(CH_3)_2]$–
18	$(CH_3)_3SiOSi[(CH_3)_2]$–	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–
19	$(CH_3)_3SiOSi[(CH_3)_2]$–	$(CH_3)_3CCH_2Si[(CH_3)_2]$–
20	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–
21	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–	$(CH_3)_3CCH_2Si[(CH_3)_2]$–
22	$(CH_3)_3CCH_2Si[(CH_3)_2]$–	$(CH_3)_3CCH_2Si[(CH_3)_2]$–

The substitution of methyl groups by ethyl (compounds **1**→**2**→**3**) increases the surface tension by about 1 mN m^{-1} per methylene unit. As the donor–acceptor contributions ($\gamma_{lv}{}^{+/-}$) decrease this continuous surface tension increase is exclusively due to considerably increased Lifshitz–van der Waals ($\gamma_{lv}{}^{LW}$) contributions. The corresponding power balance at the non-polar solid/liquid interface is generally determined by donor–acceptor contributions ($\gamma_{sl}{}^{+/-}$). Equivalent forces of this type emerge at both interfaces, although in a single case only a considerable $\gamma_{sl}{}^{LW}$ contribution has been found (compound **3**).

Aromatic hydrocarbon structures (compound **4**) increase the surface tension less efficiently (0.7 mN m^{-1} per CH-unit). However, due to the

Table 4 Dependence of the interfacial properties on the structure of the Silicon moiety

Compd	*Conc* (mol/l^{-1})	γ_{lv} (mN/m^{-1})	$\gamma_{lv}{}^{LW}$ (mN/m^{-1})	$\gamma_{lv}{}^{+/-}$ (mN/m^{-1})	γ_{sl} (mN/m^{-1})	$\gamma_{sl}{}^{LW}$ (mN/m^{-1})	$\gamma_{sl}{}^{+/-}$	α (mN/m^{-1})	cos θ	θ (deg)
1	1.0×10^{-3}	21.5	19.0	2.5	2.4	0.0	2.4	16.5	0.767	40
2	3.0×10^{-3}	22.6	22.0	0.6	0.7	0.1	0.6	18.2	0.805	36
3	1.0×10^{-3}	26.9	25.5	1.4	1.9	0.49	1.41	17.0	0.632	51
4	1.0×10^{-3}	24.9	21.5	3.4	3.5	0.1	3.4	15.4	0.618	52
5	1.0×10^{-3}	22.2	21.0	1.2	1.2	0.06	1.14	17.7	0.797	37
6	3.0×10^{-3}	23.1	21.5	1.6	1.7	0.08	1.62	17.2	0.744	42
7	3.0×10^{-3}	24.2	23.4	0.8	1.1	0.24	0.86	17.8	0.735	43
8	3.7×10^{-3}	24.0	23.1	0.9	1.1	0.2	0.9	17.8	0.741	42
9	3.0×10^{-3}	23.6	22.1	1.5	1.6	0.1	1.5	17.3	0.733	43
10	3.0×10^{-3}	24.9	23.5	1.4	1.7	0.25	1.45	17.2	0.691	46
11	1.0×10^{-3}	21.9	20.7	1.2	1.2	0.04	1.16	17.7	0.808	36
12	3.0×10^{-3}	23.7	22.5	1.2	1.4	0.2	1.2	17.5	0.738	42
13	3.0×10^{-3}	23.4	22.7	0.7	0.8	0.2	0.6	18.1	0.773	39
14	3.0×10^{-3}	24.8	24.7	0.1	0.4	0.3	0.1	18.5	0.746	42
15	1.0×10^{-2}	22.4	20.5	1.9	1.9	0.03	1.87	17.0	0.758	41
16	1.0×10^{-3}	25.0	20.6	4.4	4.4	0.04	4.36	14.5	0.580	55
17	1.0×10^{-4}	21.7	20.9	0.8	0.8	0.05	0.75	18.1	0.834	33
18	1.0×10^{-4}	23.3	22.0	1.3	1.4	0.1	1.3	17.5	0.751	41
19	1.0×10^{-4}	23.1	22.3	0.8	0.9	0.14	0.76	18.0	0.779	39
20	1.0×10^{-4}	24.8	23.9	0.9	1.2	0.3	0.9	17.7	0.714	44
21	1.0×10^{-4}	24.6	23.1	1.5	1.7	0.2	1.5	17.2	0.699	46
22	1.0×10^{-4}	25.2	24.4	0.8	1.1	0.35	0.75	17.8	0.706	45

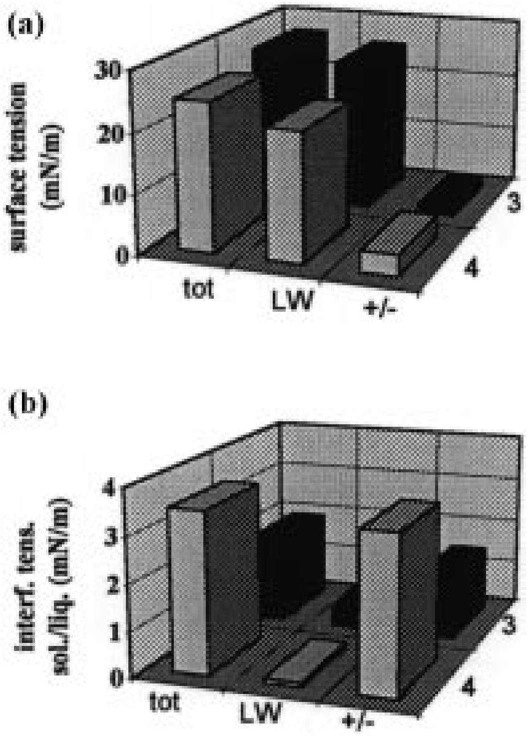
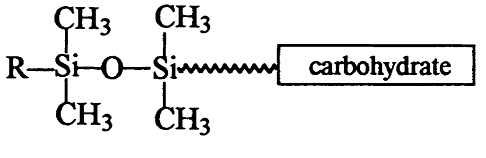


Figure 2 Surface tension (a) and solid/liquid interfacial tension (b) on FEP® of compounds **3** and **4**. Total (tot), donor–acceptor (+/−) and Lifshitz–van der Waals (LW) contributions are shown.

effect of the π-system this increase has its origin in a strengthened donor–acceptor contribution. As these donor–acceptor-type forces also emerge at the solid/liquid interface, the ability to wet the perfluorinated material is considerably reduced. Figure 2 illustrates the diverging consequences of ethyl and phenyl substitutions on siloxane backbones.

4.2 Variable substituted disiloxane structures

Somewhat surprisingly, we found practically identical data for carbohydrate surfactants of the MM* (**11**) and MDM* (**5**) type.[4] From a systematic point of view compound (**5**) is a dimethylsiloxy derivative of **11**. We argued that the second oxygen atom of the trisiloxane structure is too distant to give a noticeable energy response at the solid/liquid interface. In order to check this assumption we synthesized a series of surfactants of the general structure **A.**



$R{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}\sim\boxed{\text{carbohydrate}}$

Structure 17

As already mentioned, the substitution of the methyl group in (**11**) by a siloxanyl moiety (**5**) did not have significant energy consequences. Substitutions of the methyl group by t-butyl (**9**), neopentyl (**8**) or (t-butyl)ethyl (**10**) groups were carried out in order to insulate the Si-O-Si structure from the interface. However, the expected increases of the surface tension and its Lifshitz–van der Waals contibution are not accompanied by a continuous decrease in the donor–acceptor portion (stable 'background polarity' about 1 mN m^{-1}). The incorporation of a carbosilane moiety (**7**) does not alter this situation. As a consequence the energetic balance at the solid/liquid interface remains dominated by donor–acceptor forces. Obviously bulky substituents of the alkyl or carbosilyl type represent inadequate tools to 'insulate' disiloxane's oxygen atom from the interface (Fig. 3).

Nevertheless a comparison of the isomeric siloxane/carbosilane structures (**6**) and (**7**) shows that the substitution location has a certain effect on the interfacial properties. The terminal carbosilane (**7**) possesses the higher surface tension and is less polar. In compound (**6**) the carbosilane substructure is located in the interior. Here the terminal siloxanyl moiety can 'hide' it much better. The surface tension is lower but the force balance is shifted more to the donor–acceptor side (Fig. 4).

4.3 Polysilanes, carbosilanes and neopentyl-substituted silanes

The constant 'background polarity' of about 1 mN m^{-1} was interpreted in terms of an inability of bulky alkyl substituents to 'insulate' the siloxane structure completely from the interface. The disiloxane structure is flexible enough to orient its low-energy methyl groups (inevitably accompanied by the oxygen atom) close to the interface. If these considerations are based on realistic assumptions, derivatives without siloxane bonds should not exhibit this 'background polarity'.

Compounds (**13**) and (**14**) represent a carbosilane and a neopentylsilane derivative respectively. The stepwise surface tension increase (compounds **11** → **13** → **14**) is accompanied by a steadily declining donor–acceptor contribution. For compound (**14**) a

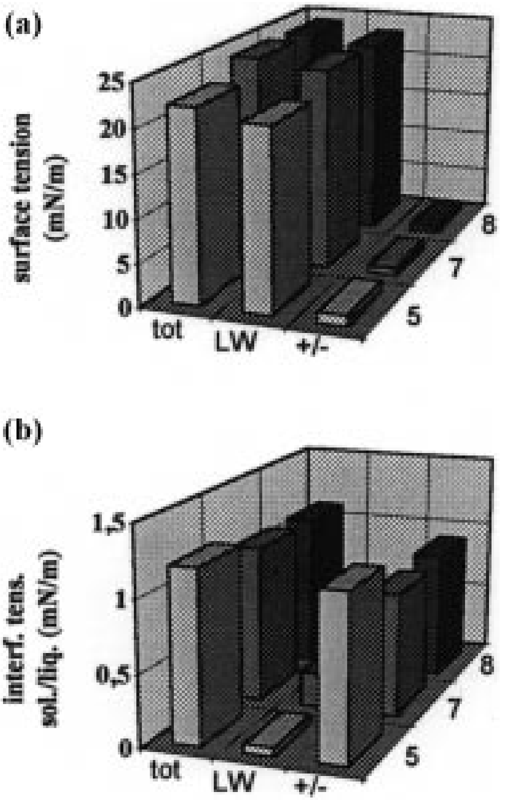


Figure 3 (a) Surface tension and (b) solid/liquid interfacial tension on FEP® of compounds **5**, **7** and **8**. Total (tot), donor–acceptor (+/−) and Lifshitz–van der Waals (LW) contributions are shown.

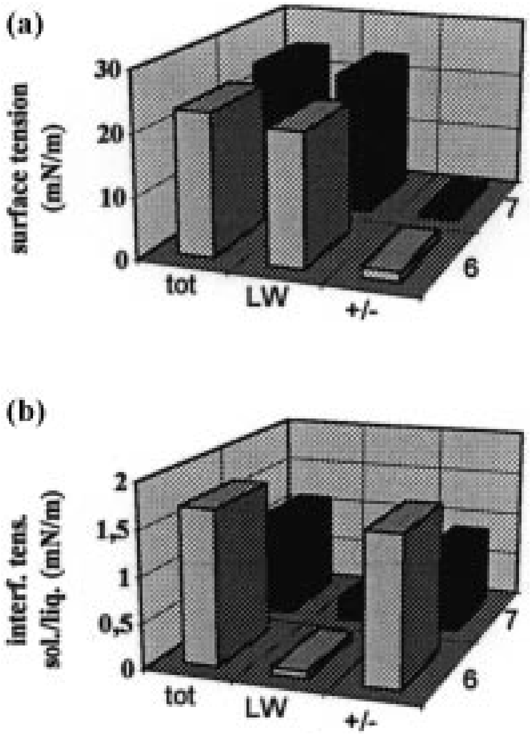


Figure 4 Surface tension and solid/liquid interfacial tension on FEP® of compounds **6** and **7**. Total (tot), donor–acceptor (+/−) and Lifshitz–van der Waals (LW) contributions are shown.

donor–acceptor contribution was practically not observed. It is noteworthy that this compound is the only case where the solid/liquid interfacial tension was determined by the Lifshitz–van der Waals force (Fig. 5). Despite the presence of a bulky carbohydrate moiety and the huge amount of water in the bulk phase, the perfluorinated material 'feels' exclusively a hydrocarbon structure.

Although there is so far no independent proof Fig. 6 shows possible orientations of selected surfactant molecules at the solid/liquid interface. The fact that for the neopentyl-substituted silane derivative **14** practically no donor–acceptor contribution was found immediately raises the question of the range of these forces at interfaces.

Diverging from Oss et al.,[23] we include in 'donor–acceptor forces' all those types which are based on long-term uneven distributions of electrons.[20–22] It is well established[24] that dipole–dipole interactions (for example) have a short-range character. Short-term uneven distributions of electrons (fluctuations on a quantum-mechanical time scale) are the source of non-polar Lifshitz–van der Waals forces.

Nevertheless only a few experimental data are available in the literature demonstrating the consequences of the distance decay of certain force types in real wetting situations. As early as 1962 Shafrin and Zisman[25] investigated the wetting behaviour of n-alkanes and certain polar liquids on monolayers of partially fluorinated fatty acids. He found that the surface energy of monolayers remains constant if the seven terminal C-atoms are fluorinated. In his case the depth influence of the -CF_2CH_2-dipole has a maximum range of 7.5 Å. Whitesides[26] found that in the course of systematic wetting experiments with long-chained ether monolayers the polar influence of the ether oxygen atom (-CH_2OCH_2-) could be detected over a distance of 2 Å for hexadecane and 5 Å for water.

Considering (1) the polarity differences for the branched (**1**) and straight-chained (**5**) trisiloxanyl

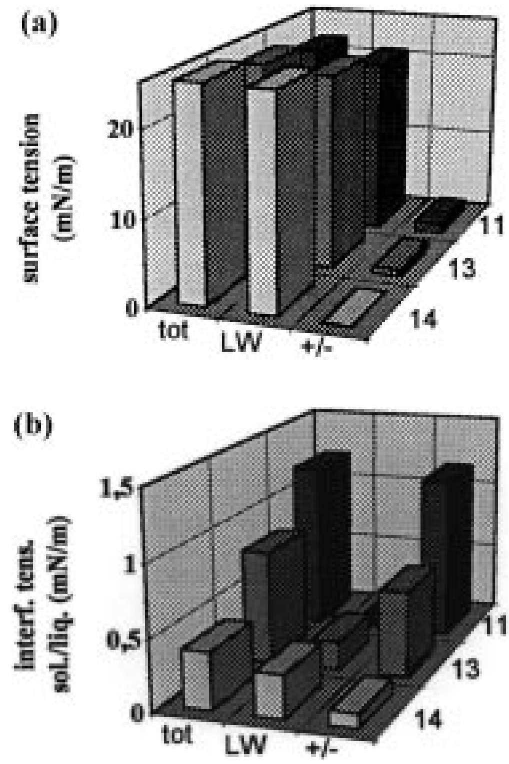


Figure 5 Surface tension and solid/liquid interfacial tension on FEP® of compounds **11, 13** and **14**. Total (tot), donor–acceptor (+/−) and Lifshitz–van der Waals (LW) contributions are shown.

structures, (2) the practical identity of the energy data for the disiloxane **11** and the trisiloxane derivative (**5**) (3) the strong donor–acceptor contributions for the 'inner' carbosilane (**6**) and (4) the non-polar character of the neopentyl-substituted silane derivative (**14**), it is reasonable to assume that the range of donor–acceptor forces is restricted to one Si-O-Si moiety.

For compound (**5**) (Fig. 6; Table 5) we calculated a maximum range of donor–acceptor forces of about 4.5 Å. This means that at the solid/surfactant solution interface the adjustment of the equilibrium energy balance proceeds at a submolecular level. For the silicon-containing surfactant type under investigation, spacer and hydrocarbon unit are too distant from the interface. They act as necessary tools to orient the silicon-containing hydrophobe but do not significantly influence the interfacial energy.

We are well aware that the validity of this last statement is restricted to a given spacer and carbohydrate moiety configuration. Energy influences of different spacer structures, carbohydrates and modifying elements have been examined in detail previously.[4] Additionally, in certain cases a measurable steric/packing influence[25] may exist. Usually siloxane surfactants consist of a bulky silicon-containing hydrophobe and a smaller hydrophilic moiety. An example is compound (**1**). Here a trisiloxane unit (50 Å^2 area per unit at the liquid/vapour interface) is connected with a smaller saccharide moiety (30–35 Å^2 per unit) (Fig. 7). The siloxane block can cover the solid surface. The

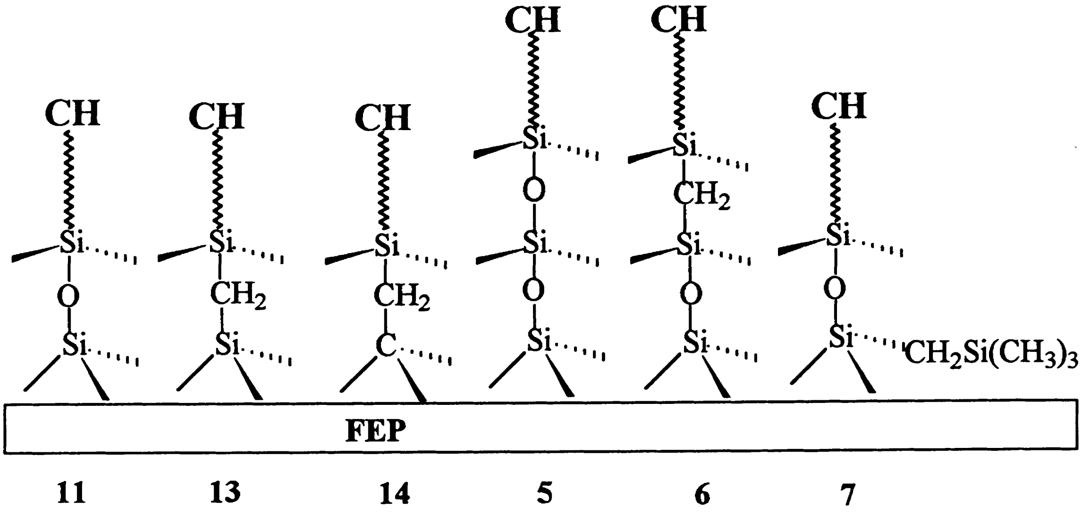


Figure 6 Possible orientations of selected silicon-containing hydrophobes on FEP®.

Table 5 Bond angles and bond distances[27–29] of permethylated compounds $(CH_3)_3$ **YXY** $(CH_3)_3$

Structure	Angle **YXY** (deg)	Distance **X–Y** (Å)	Distance **Y**–CH_3 (Å)
$(CH_3)_3$ **SiOSi** $(CH_3)_3$	148.8	1.626	1.850
$(CH_3)_3$**SiCH$_2$Si**$(CH_3)_3$	123.2	1.889	1.874
$(CH_3)_3$**SiSi**$(CH_3)_3$	—	2.340 (Si–Si)	1.877
$(CH_3)_3$**CCH$_2$C**$(CH_3)_3$	128.0	1.545	1.545

Table 6 Energy classification of the surfactants under investigation

Subgroup	Energetic Profile	Structures	Examples
I	Low γ_{lv} and low to medium γ_{sl}	Straight-chained and permethylated siloxane derivatives	**5, 11, 17**
II	High γ_{lv} and low to medium γ_{sl}	Not-permethylated siloxane surfactants, carbosilane and branched silane derivatives	**3, 8, 13, 14**
III	High γ_{lv} and high γ_{sl}	Aromatic substituents containing siloxane derivatives and surfactants bearing extreme bulky hydrophiles	**4, 16**

opposite case is represented by compound **16** (for chemical structure, see section 2.1). The trisiloxane moiety is connected with two saccharide units. An exclusive coverage of the solid by low-energy siloxane structures is impossible and the measured interfacial energy as well as its donor–acceptor contribution increases.

4.4 Branched structures

The results for branched structures are less clear-cut. The data for the double-chained derivative (**17**) is closely related to that of the single-chained one (**11**). Successive substitutions of the disiloxane moiety by carbosilanes and neopentyl-substituted silanes yield increased surface tensions. For unknown reasons their donor–acceptor contributions show an unsystematic scattering. The same is true for the solid/liquid interfacial tension.

Nevertheless there is a steady shift of the ratio of both contributions towards the Lifshitz–van der Waals side with increasing substitution of the siloxanyl moieties. The derivatives become more and more hydrocarbon-like.

4.5 Surface tension, solid/liquid interfacial tension and contact angle

In Sections 4.1–4.4 we discussed in detail the influence of different types of silicon-containing hydrophobes on the liquid/vapour and solid/liquid interfacial energies. Apart from chemical structure differences, the surfactants under investigation can be divided qualitatively into certain energy subgroups (Table 6).

An immediate consequence of the existence of subgroup II is that the disputed ‘equation of state’ concept[30,31] does not hold for solutions of silicon-containing surfactants (Fig. 8). The reason has

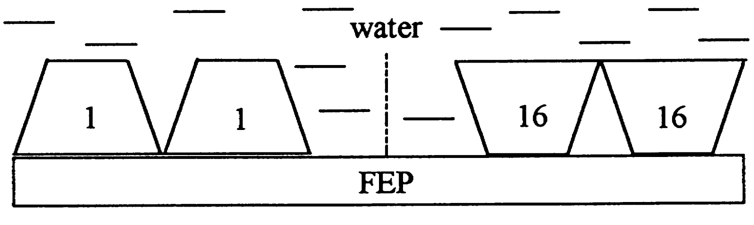


Figure 7 Schematic representation of the surface coverage by surfactants of different shapes.

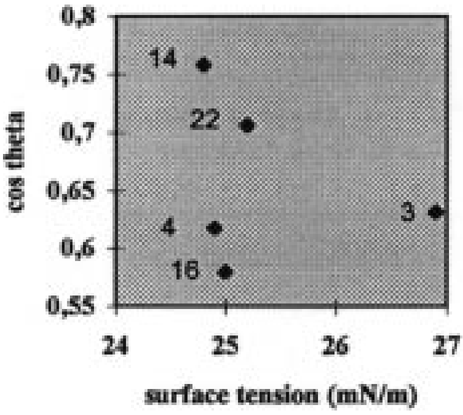


Figure 8 Surface tensions and contact angles (cos θ) for solutions of selected silicon-containing surfactants.

already been examined.[14] Lifshitz–van der Waals and donor–acceptor forces are treated in different ways at the liquid/vapour and non-polar solid/liquid interfaces. Equivalent donor–acceptor forces emerge at both interfaces. Lifshitz–van der Waals forces dominate the liquid/vapour energy balance but usually play a minor role at the non-polar solid/liquid interface.

It is noteworthy that the deviations from the 'equation of state' concept are more pronounced for surfactant solutions than for the corresponding precursors.[5] We believe that two properties of surfactant solutions are responsible for this effect. Due to the influence of the bulk water, surfactant, adsorption layers are highly oriented. Additionally, as there is a 'geometrical argument' that surfactant molecules possessing an unfavourable geometry (see the difference between compounds **1** and **16** in Fig. 7) cannot cover the solid surface with their most hydrophobic sites alone. Other substructures or water have to fill the 'holes' and cause high interfacial tensions.

The data discussed in this paper were generated from equilibrium wetting experiments. This methodology had to be applied in order to obtain a comprehensive insight into the complex relationship between chemical structure and interfacial energy.

However, we are well aware that (a) in the majority of industrial wetting processes dynamic steps are included, and (b) therefore the surfactant concentration at the three-phase contact is neither constant nor necessarily above the cmc. For that reason we will discuss in separate papers the concentration dependence of the wetting properties and an approach to the quantitative characterization of the dynamic wetting behaviour.

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REFERENCES

1. T. Stoebe, Z. Lin, R. M. Hill, M. D. Ward and H. T. Davis, *Langmuir* **12**, 337 (1996).
2. K. P. Ananthapadmanabhan, E. D. Goddard and P. Chandar, *Colloid Surf.* **44**, 281 (1990).
3. S. Zhu, W. G. Miller, L. E. Scriven and H. T. Davis, *Colloid Surf.* **90**, 63 (1994).
4. F. Tiberg and A. M. Cazabat, *Europhys. Lett.* **25**, 205 (1994).
5. F. Tiberg and A. M. Cazabat, *Langmuir* **10**, 2301 (1994).
6. T. Svitova, H. Hoffmann and R. M. Hill, *Langmuir* **12**, 1712 (1996).
7. H. Haidara, M. K. Chaudhury and M. J. Owen, *J. Phys. Chem.* **99**, 8681 (1995).
8. R. Wagner, L. Richter, R. Wersig, G. Schmaucks, B. Weiland, J. Weißmüller and J. Reiners, *Appl. Organometal Chem.* **10**, 421 (1996).
9. R. Wagner, L. Richter, B. Weiland, J. Weißmüller and J. Reiners, *Appl. Organometal. Chem.* **10**, 437 (1996).
10. R. Wagner, L. Richter, B. Weiland, J. Weißmüller, J. Reiners and W. Krämer, *Appl. Organometal. Chem.* **11**, 523 (1997).
11. R. Wagner, L. Richter, J. Weißmüller, J. Reiners, K.-D. Klein, D. Schaefer and S. Stadtmüller, *Appl. Organometal. Chem.* **11**, 617 (1997).
12. R. Wagner, L. Richter, Y. Wu, J. Weißmüller, J. Reiners, E. Hengge, A. Kleewein and K. Hassler, *Appl. Organometal. Chem.* **11**, 645 (1997).
13. R. Wagner, L. Richter, Y. Wu, B. Weiland, J. Weißmüller, J. Reiners, E. Hengge and A. Kleewein, *Appl. Organometal. Chem.*, **12**, 47 (1998).
14. T. Young, *Phil. Trans. R. Soc. London* **95**, 65 (1805).
15. W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.* **52**, 1751 (1930).
16. G. Czichocki, B. Gilsenbach, M. Olschewski and L. Richter, *Plast. Kautsch.* **34**, 445 (1987).
17. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.* **13**, 1741 (1969).
18. F. M. Fowkes, *Ind. Eng. Chem.* **56**, 40 (1964).
19. H. Maki, S. Saeki, I. Ikeda and S. Komori, *J. Am. Oil Chem. Soc.* **46**, 635 (1969).
20. R. Menescal and R. West, *Macromolecules.* **24**, 329 (1991).
21. T. Fujisaka and R. West, *J. Organometal. Chem.* **449**, 105 (1993).

22. K. Oka, N. Fujiue, S. Nakanishi, T. Takata, T. Dohmaru, C.-H. Yuan and R. West, *Chem. Lett.* 875 (1995).
23. C. J. van Oss, M. K. Chaudhury and R. J. Good, *Chem Rev* **88**, 927 (1988).
24. J. N. Israelashvili, *Intermolecular and Surface Forces*, 2nd edn, Academic Press, London, 1991, p. 59.
25. E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.* **66**, 740 (1962).
26. C. D. Bain and G. M. Whitesides, *J. Am. Chem. Soc.* **110**, 5897 (1988).
27. M. J. Barrow, E. A. V. Ebsworth and M. M. Harding, *Acta Crystallogr. B.* **35**, 2093 (1979).
28. S. Patei and Z. Rappoport, *The Chemistry of Organic Silicon Compounds*, John Wiley, New York, 1989, p. 248.
29. B. Beagley, J. J. Monaghan and T. G. Hewitt, *J. Mol. Struct.* **8**, 401 (1971).
30. O. Driediger, A. W. Neumann and P. J. Sell, *Kolloid Zeit. Zeit. Polym.* **201**, 52 (1965).
31. O. Driediger, A. W. Neumann and P. J. Sell, *Kolloid Zeit. Zeit. Polym.* **204**, 101 (1965).