APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 645–657 (1997)

Silicon-Modified Carbohydrate Surfactants V: The Wetting Behaviour of Low-Molecular-Weight Siloxane, Carbosilane, Silane and Polysilane Precursors on Low-Energy Surfaces

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The surface tensions, wetting tensions, contact angles and solid/liquid interfacial tensions of defined siloxanes as well as those of analogous carbosilanes, polysilanes and neopentyl substituted silanes were determined. The wetting experiments were carried out on a glass plate coated with perfluoroalkyl methacrylate (FC 722®). The siloxanes possess the lowest surface tensions. Due to the presence of oxygen atoms in the siloxane backbone, a donor–acceptor portion ($\gamma_{lv}^{+/-}$) of the surface tension of about 1–2 mN/m was determined. The solid/liquid interfacial tension also contains a donor–acceptor portion ($\gamma_{sl}^{+/-}$). Its value is almost identical to that of $\gamma_{lv}^{+/-}$. The $\gamma_{sl}^{+/-}$ differences between individual molecules of the same surface tension are responsible for contact angle differences of up to 4°. © 1997 by John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 645–657 (1997)
No. of Figures: 6 No. of Tables: 8 No. of Refs: 50

Keywords: siloxane; surface tension; control angle; interfacial tension; wetting tension

Received 7 May 1996; accepted 15 September 1996

1 INTRODUCTION

Due to their extremely low surface tension, permethylated siloxane surfactants remain surface-active in many hydrocarbon-based organic liquids. This property has led to their broad application in the extensively studied polyurethane foaming process. The closely related ability to wet low-energy hydrocarbon-based solid surfaces has led to applications in certain plant protection formulations.[1] Structurally this surface activity is founded on the combination of accumulated low-energy methyl groups[2] and unusually flexible –Si–O–Si– bonds (measured bond angles[3] between 105 and 180°) in the siloxanyl moiety.

Although not well understood, this backbone flexibility seems to be due to an additional electron density transfer from oxygen's lone pairs into the covalent Si–O bond region yielding a widened Si–O–Si bond angle and a shortened Si–O bond length.[4,5] Increased electron densities and widened bond angles accompanied by shortened bond lengths suggest that the driving force is not a polarity increase, but rather an emerging π-bonding component caused by the 3p- or 3d-orbitals of the silicon atom.[6] The participation of the latter is supported by X-ray emission data.[6] On the other hand, orbital size calculations lead to the conclusion that the silicon 3d-orbitals cannot contribute to a hypothetical (2p–3d) π-bond.[7]

From an interfacial energy point of view these qualitative factors yield an apparently contradictory result. On the one hand, it has been known for a long time that the incorporation of non-polar $-CH_2-$ moities or polar oxygen atoms

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Contract grant sponsor: German Ministry for Research and Technology; Contract grant number: 0310317 A/B.
Contract grant sponsor: Deutsche Forschungsgemeinschaft; Contract grant number: WA 1043/1-1.

CCC 0268–2605/97/080645–13 $17.50

Table 1 Surface tensions γ_{lv} of selected hydrocarbon derivatives

Compound	Structure	Surface tension at 20 °C (mN/m)	Ref.
n-Octane	C_4H_9–C_4H_9	21.8	9
n-Nonane	C_4H_9–$\mathbf{CH_2}$–C_4H_9	22.9	8
Di(n-butyl) ether	C_4H_9–**O**–C_4H_9	22.8	8
2-Octanol	$CH_3CH(\mathbf{O}H)(CH_2)_5CH_3$	26.7	9
1-Octanol	$H\mathbf{O}CH_2(CH_2)_6CH_3$	27.8	9

into hydrocarbon structures leads to increased surface tensions[8, 9] reflecting stronger intermolecular interactions (Table 1). The 'effectivity' of the surface tension increase depends strongly on the bond type created by the oxygen atom. After incorporation of longer alkyl substituents into conventional,[10] or even–CF_3 moieties bearing siloxanes,[11] the same trend was observed. On the other hand, it had already been demonstrated for aqueous surfactant solutions[12] that the change from permethylated polysilanyl (–Si–Si–) to analogous siloxanyl (–Si–O–Si–) backbones yields a considerable reduction of the surface tension (Table 2), indicating a reversed effect of oxygen atoms in silicon-containing structures.

Recognizing that both surface activities (liquid/vapour and solid/liquid) are responsible for the spreading of a surfactant solution drop on a given solid material, we have reported on an attempt to quantify the influence of siloxanyl moieties on the wetting properties of carbohydrate surfactants by surface tension as well as wetting tension measurements.[13]

A description of the interfacial properties of siloxanyl-substituted surfactants by wetting experiments remains incomplete without an investigation of the precursor molecules. These precursors differ from the surfactant molecules by the absence of the bulky, hydrophilic substituent. A notable consequence is the lower degree of orientation at interfaces.

Additionally, these silicon-containing liquids could help to solve an apparently simple but nevertheless long-standing problem of the wetting process. The question whether the macroscopic contact angle θ of a liquid in the three-phase system liquid–solid–vapour (Fig. 1) strictly depends on the surface tension γ_{lv} (σ) or reflects the superposition of the surface tension and the solid/liquid interfacial tension γ_{sl}, both independent of each other, is still disputed (Young equation,[14] Eq. [1]):

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

where γ_{sv} is the solid surface tension and α is the wetting tension.

One source of uncertainty arises from the sensitivity of the system itself. Solid surface roughness,[15, 16] temperature[17, 18] and drop size deviations[19, 20] can influence the results considerably. Another one arises from the energy properties of the liquids. For liquids of the same surface tension, variations in the contact angles on a given solid substrate, if they exist, have to have their origin in considerably different polarities of the molecules. Strictly non-polar, liquid hydrocarbons cover the surface tension range from about 15 mN/m (n-pentane) to 27 mN/m (n-hexadecane.[21]The lower limit for the surface tension of sufficiently polar organic liquids (i.e. alkanols like n-butanol[21] or methanol[22]) is about 23 mN/m. As a result there is only the narrow surface tension range from 23 mN/m to 27 mN/m to carry out experiments with hydrocarbon-based liquids.

Table 2 Surface tensions γ_{lv} of aqueous solutions of different silicon-containing surfactants[12]

Structure	Concn (mol/l)	Surface tension (mN/m)
$(CH_3)_3\mathbf{SiSi}[(CH_3)_2](CH_2)_3(OCH_2CH_2)_4H$	5×10^{-3}	26
$(CH_3)_3\mathbf{SiOSi}[(CH_3)_2](CH_2)_3(OCH_2CH_2)_4H$	5×10^{-3}	23

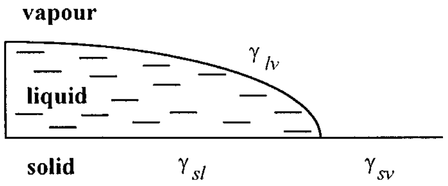


Figure 1 Drop on a solid surface.

The incorporation of polar siloxanes into the substance spectrum widens the accessible range down to about 15 mN/m. This practice should have another advantage. As it is known that the donor–acceptor portion of the surface tension even for highly polar organic liquids (like lower alkanols) is small compared to the complementary Lifshitz–van der Waals component, a significant reduction of the total surface tension should increase the relative influence of donor–acceptor interactions.

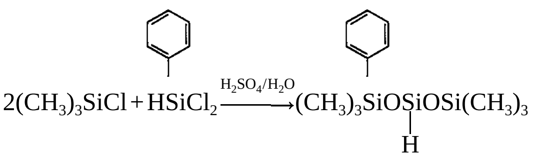
Therefore it is the purpose of this paper to provide a comprehensive, structure-related, quantitative description of the wetting behaviour of typical structures containing silicon atoms, namely (i) siloxanes [≡Si–O–Si≡], (ii) carbosilanes [≡Si–CH_2–Si≡], (iii) polysilanes [≡Si–Si≡] and (iv) silanes [≡Si–CH_2–C≡].

2 MATERIALS AND METHODS

2.1 Materials

The wetting behaviour of the silicon-containing liquids listed in Table 3 has been investigated.

Compounds **2**–**4** and **11** are commercially available (ABCR). The synthesis of compounds **1**, **5**, **8**, **9** and **10** by chlorosilane hydrolysis and equilibration has been described in a preceding paper.[23] The siloxanes **6** and **7** have also been synthesized by a combination of chlorosilane hydrolysis and acid-catalysed equilibration (Eqn [2]). Thus, under argon 13.7 g (7.75×10^{-2} mol) $C_6H_5Cl_2SiH$, 100 ml $(CH_3)_3SiCl$ and 50 ml $(CH_3)_3SiOSi(CH_3)_3$ (MM) were mixed. The mixture was dropped into a stirred dispersion of 50 ml MM in 116 ml sulphuric acid (80% by wt) at room temperature during 0.5 h. After 2 h of stirring the siloxane layer was separated and washed seven times with deionized water. $NaHCO_3$ (5 g) was added for 12 h. The solid was filtered off and compound **8** isolated by vacuum distillation (127 °C/32 mmHg, 5.7 g).

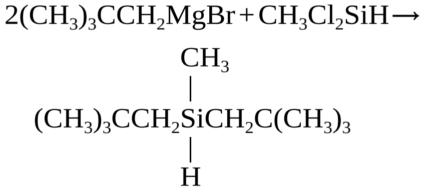


$$2(CH_3)_3SiCl + HSiCl_2 \xrightarrow{H_2SO_4/H_2O} (CH_3)_3SiO\underset{H}{Si}OSi(CH_3)_3$$ [2]

The carbosilanes **12**, **13**, **15**, **16** and **17** were synthesized from $(CH_3)_3SiCH_2Cl$ via a Grignard route.[24–26] Compound **14** can be synthesized from **13** by chlorination and subsequent hydrogenation (Scheme 1). Thus, 6.24 g Mg turnings (2.6×10^{-1} mol) and 20 mg I_2 were placed under argon in a three-necked bottle equipped with a refluxing condenser and two dropping funnels, to which 20 ml dry tetrahydrofuran (THF) and subsequently 1.5 g $(CH_3)_3SiCH_2Cl$ were added. The reaction started immediately; 180 ml THF were added and during 2 h 28.5 g $(CH_3)_3SiCH_2Cl$ (all together 30 g, 2.44×10^{-1} mol) were dropped in, keeping the solvent refluxing. To complete the reaction this temperature was maintained for 1 h. Afterwards $(CH_3)_2SiCl_2$ (16.4 g, 1.3×10^{-1} mol) was dropped into the refluxing solution during 1 h and this temperature was maintained for 9 h. The precipitated salt was filtered off from the THF solution and the salt extracted with n-pentane. The THF solution and the extract were united and after distillation 8.4 g $(CH_3)_3SiCH_2Si[(CH_3)_2)]CH_2Si(CH_3)_3$ (**13**; b.p. 94 °C/15 mmHg) were obtained.

To chlorinate this product, 34.6 g (1.56×10^{-1} mol) of **13** and an equimolar amount of $AlCl_3$ were mixed under argon and cooled to 0 °C. During 1 h 12.3 g acetyl chloride (1.59×10^{-1} mol) was added. Afterwards the temperature is raised to 60 °C for 1 h and a two-phase system emerged. The upper layer was separated and 12.2 g (4.82×10^{-2} mol) $(CH_3)_3SiCH_2Si[(CH_3)_2)]CH_2Si(CH_3)_2Cl$ was isolated by distillation (81–83 °C/8 mmHg). The chlorinated carbotrisilane was dropped into a cooled (0 °C) suspension of 1.2 g $LiAlH_4$ in 70 ml dry THF. The mixture was heated to room temperature for 1 h. Afterwards the volatile substances were evaporated off. By distillation 6 g $(CH_3)_3SiCH_2Si[(CH_3)_2)]CH_2Si(CH_3)_2H$ (b.p. 80–82 °C/12 mmHg) could be isolated.

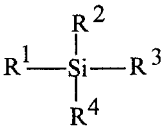
In complete analogy to the Grignard-type procedure described above, the neopentyl-substituted silanes **25** and **26**[27, 28] were synthesized from $(CH_3)_3$ CCH_2Br[29] (Eqn [3])



$$2(CH_3)_3CCH_2MgBr + CH_3Cl_2SiH \rightarrow (CH_3)_3CCH_2\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}CH_2C(CH_3)_3 \qquad [3]$$

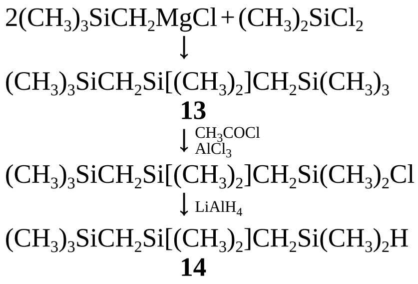
The di-, tri- and tetra-silanes **18**–**22** and **24** were synthesized from chlorosilanes by a sequence including dehalogenating reductions, halogenations and hydrogenations[30–33] (Scheme 2). Thus, in a 200 ml three-necked bottle equipped with stirrer, refluxing condenser and dropping funnel, 700 ml dry THF was placed and 34 g (4.85 mol) lithium powder was added under argon. During 5 h a mixture of 408 g (3.76 mol) $(CH_3)_3SiCl$ and

Table 3 Silicon-containing liquids investigated



No.	R^1	R^2	R^3	R^4	B.p. (°C/mmHg)	ρ (at 20 °C) (g/dm^3)
Siloxanes						
1	H	CH_3	$OSi(CH_3)_2H$	CH_3	69/760	0.753
2	H	CH_3	$OSi(CH_3)_3$	CH_3	86/760[a]	0.756
3	CH_3	CH_3	$OSi(CH_3)_3$	CH_3	99/760[a]	0.771
4	H	CH_3	$OSi[(CH_3)_2]OSi(CH_3)_3$	CH_3	134/760[a]	0.817
5	H	$OSi(CH_3)_3$	CH_3	$OSi(CH_3)_3$	142/760	0.818
6	H	$OSi(CH_3)_3$	C_2H_5	$OSi(CH_3)_3$	18/50	0.824
7	H	$OSi(CH_3)_3$	C_6H_5	$OSi(CH_3)_3$	127/30	0.951
8	H	$OSi(CH_3)_3$	$OSi(CH_3)_3$	$OSi(CH_3)_3$	55/7	0.849
9	H	$OSi(CH_2H_5)_3$	CH_3	$OSi(CH_2H_5)_3$	126–127/10	0.865
10	—	—	$-[OSi(CH_3)_2]_4-$	—	173–176/760	0.995
11	—	—	$-[OSi(CH_3)_2]_5-$	—	101/20[a]	0.959
Carbosilanes						
12	H	CH_3	$CH_2Si(CH_3)_3$	CH_3	62–63/110	0.742
13	CH_3	CH_3	$CH_2Si(CH_3)_3$	CH_3	69/110	0.754
14	H	CH_3	$CH_2Si[(CH_3)_2]CH_2Si(CH_3)_3$	CH_3	80–82/12	0.786
15	CH_3	CH_3	$CH_2Si[(CH_3)_2]CH_2Si(CH_3)_3$	CH_3	94/15	0.807
16	H	$CH_2Si(CH_3)_3$	CH_3	$CH_2Si(CH_3)_3$	97/26	0.789
17	H	$CH_2Si(CH_3)_3$	$CH_2Si(CH_3)_3$	$CH_2Si(CH_3)_3$	81–82/8	0.881
Polysilanes						
18	H	CH_3	$Si(CH_3)_2H$	CH_3	83–85/760	0.718
19	H	CH_3	$Si(CH_3)_3$	CH_3	97–100/760	0.723
20	CH_3	CH_3	$Si(CH_3)_3$	CH_3	110–112/760	0.725
21	H	CH_3	$Si[CH_3)_2]Si(CH_3)_2H$	CH_3	71/57	0.774
22	H	CH_3	$Si[(CH_3)_2]Si(CH_3)_3$	CH_3	66/20	0.777
23	H	$Si(CH_3)_3$	CH_3	$Si(CH_3)_3$	50–55/10	0.771
24	H	$Si(CH_3)_3$	$Si(CH_3)_3$	$Si(CH_3)_3$	98/10	0.812
Silanes						
25	H	CH_3	$CH_2C(CH_3)_3$	CH_3	100/760	0.718
26	H	$CH_2C(CH_3)_3$	CH_3	$CH_2C(CH_3)_3$	110–113/34	0.813
Mixed structures						
27	H	CH_3	$OSi[(CH_3)_2]CH_2Si(CH_3)_3$	CH_3	96/75	0.856
28	H	CH_3	$CH_2Si[(CH_3)_2]OSi(CH_3)_3$	CH_3	90–92/75	0.809

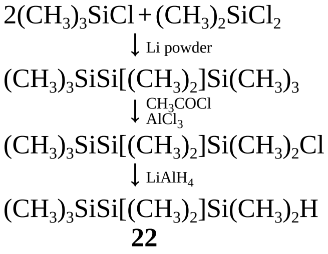
[a] Taken from ABCR catalogue (1994/95), substances P 0100, H 7310, H 7010.



$$\begin{array}{c} 2(CH_3)_3SiCH_2MgCl + (CH_3)_2SiCl_2 \\ \downarrow \\ (CH_3)_3SiCH_2Si[(CH_3)_2]CH_2Si(CH_3)_3 \\ \mathbf{13} \\ \downarrow \substack{CH_3COCl \\ AlCl_3} \\ (CH_3)_3SiCH_2Si[(CH_3)_2]CH_2Si(CH_3)_2Cl \\ \downarrow LiAlH_4 \\ (CH_3)_3SiCH_2Si[(CH_3)_2]CH_2Si(CH_3)_2H \\ \mathbf{14} \end{array}$$

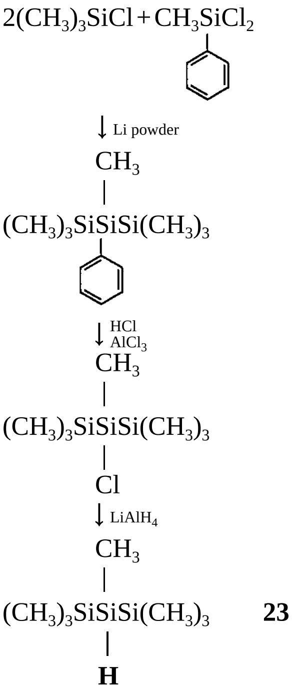
Scheme 1

149 g (1.15 mol) $(CH_3)_2SiCl_2$ was carefully dropped in. After 50% addition the initially vigorous reaction slowed down and the mixture had to be heated to maintain solvent reflux. To complete the reaction, the reflux temperature was maintained for an additional 30 h. Solids were removed by filtration under argon and $(CH_3)_3Si$-$Si[(CH_3)_2)]Si(CH_3)_3$ could be isolated from the THF solution by distillation (71.5 g, b.p. 57–63 °C/15 mmHg). The trisilane (71.5 g, 3.5×10^{-1} mol) and $AlCl_3$ (27.33 g, 3.5×10^{-1} mol) were mixed under nitrogen and cooled to 10 °C. During 1 h acetyl chloride (46.6 g, 3.5×10^{-1} mol) was added. A two-phase system emerged. Due to the exothermic reaction, despite cooling, the temperature rose to 30 °C. Afterwards the mixture was heated to 60 °C for 1 h. With a syringe the upper silane layer was removed. After distillation under nitrogen a mixture of $Cl(CH_3)_2SiSi[(CH_3)_2]Si(CH_3)_2Cl$ and $Cl(CH_3)_2SiSi[(CH_3)_2]Si(CH_3)_3$ (37 g, b.p. 70–81 °C/15 mmHg, ratio 20 : 80) was obtained. This trisilane mixture (37 g, $\approx 1.6 \times 10^{-1}$ mol Cl) was cooled under nitrogen to 0 °C and during 1 h a 2 M solution of $LiAlH_4$ in diethyl ether (40 ml, 8×10^{-2} mol, 2H) was added. The volatile products were condensed off. Repeated distillations under reduced pressure yielded 8 g $(CH_3)_3Si$-$Si[(CH_3)_2]Si(CH_3)_2H$ (b.p. 66–68 °C/30 mmHg) and 4.4 g $H(CH_3)_2SiSi[(CH_3)_2]Si(CH_3)_2H$ (**22**; b.p. 71 °C/57 mmHg).



$$\begin{array}{c} 2(CH_3)_3SiCl + (CH_3)_2SiCl_2 \\ \downarrow \text{Li powder} \\ (CH_3)_3SiSi[(CH_3)_2]Si(CH_3)_3 \\ \downarrow \substack{CH_3COCl \\ AlCl_3} \\ (CH_3)_3SiSi[(CH_3)_2]Si(CH_3)_2Cl \\ \downarrow LiAlH_4 \\ (CH_3)_3SiSi[(CH_3)_2]Si(CH_3)_2H \\ \mathbf{22} \end{array}$$

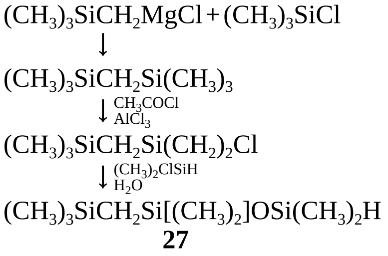
Scheme 2



Scheme 3

The trisilane **23** was synthesized from a phenylated derivative according to a literature procedure[34] (Scheme 3).

The mixed structure **27**[35] can be synthesized by a combination of halogenation and acid-catalysed hydrolysis (Scheme 4). Thus 40 g (2.37×10^{-1} mol) $(CH_3)_3SiCH_2Si(CH_3)_3$ was monochlorinated in analogy to the procedure described for compound **13**; 37 g $(CH_3)_3Si$-$CH_2Si(CH_3)_2Cl$ was obtained, of which 30 g (1.77×10^{-1} mol) and 10 g (1.27 mol) $(CH_3)_2ClSiH$ were mixed in a dropping funnel and dropped into agitated 50% by wt sulphuric acid (850 ml) (care!). The organic layer was separated after 5 h, washed five times with deionized water, dried and neutralized with $NaHCO_3$. Distillation yielded 6 g $(CH_3)_3SiCH$-



$$\begin{array}{c} (CH_3)_3SiCH_2MgCl + (CH_3)_3SiCl \\ \downarrow \\ (CH_3)_3SiCH_2Si(CH_3)_3 \\ \downarrow \substack{CH_3COCl \\ AlCl_3} \\ (CH_3)_3SiCH_2Si(CH_2)_2Cl \\ \downarrow \substack{(CH_3)_2ClSiH \\ H_2O} \\ (CH_3)_3SiCH_2Si[(CH_3)_2]OSi(CH_3)_2H \\ \mathbf{27} \end{array}$$

Scheme 4

$_2Si(CH_3)_2OSi(CH_3)_2H$ (**37**; b.p. 96 °C/75 mmHg).

Compound **28**[35, 36] was synthesized from $H[CH_3)_2]SiCH_2MgCl$ and $(CH_3)_3SiOSi(CH_3)_2Cl$ in a Grignard-type reaction (Eqn [4]).

$$(CH_3)_2HSiCH_2MgCl \xrightarrow{(CH_3)_3SiOSi(CH_3)_2Cl}$$

$$\underset{\mathbf{28}}{(CH_3)_3SiOSi[(CH_3)_2]CH_2Si(CH_3)_2H} \qquad [4]$$

The C_5–C_{16} n-alkanes (99+ quality, Aldrich) and *cis*-decahydronaphthalene (*cis*-decalin, >98%, Fluka) are commercially available and were used without further purification.

2.2 Methods

Contact angles θ of the silicon-containing liquids on a glass plate covered with a perfluoroalkyl methacrylate polymer (FC 722®, 3M Corp.) were determined by independent measurements of the surface tension γ_{lv} (ring method) and wetting tension α (Wilhelmy method) (Eqn [1]). Each measurement was carried out at 20 °C. Equipment and procedure details have been explained in a preceding paper.[13]

To measure the wetting tension α, the polymer-covered glass plate of defined width and thickness (2.190 cm × 0.0145 cm) was dipped stepwise (usually 0.1 cm, 0.1 cm/min) into the liquid with an accuracy of 0.001 cm. The force p measured correlates with α according to Eqn [5].

$$p=u\alpha+(-)r\boldsymbol{g}dbx_e \qquad [5]$$

where

u = perimeter of the FEP® plate
r = liquid density
$\boldsymbol{g}$ = 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 the force immediately and after 1 min. This time was found to be necessary for the system to reach an equilibrium state of wetting. Plotting the 1-min values of the force p against the immersion depth x_e yields, by extrapolation to $x_e = 0$, the wetting tension α.

The surface tensions γ_{lv} of the liquids were determined by exchanging the covered glass plate for a Pt–Ir ring. The surface tension values obtained were corrected according to Harkins and Jordan.[37]

To extract the interfacial tension solid/liquid γ_{sl} from the wetting tension α (Eqn [1]), the solid surface tension γ_{sv} of the FC 722®-covered glass plate has been determined from surface tension γ_{lv} and contact angle θ measurements on a series of strictly non-polar n-alkanes. The approaches of van Oss[38] (Eqn [6]) and Neumann[39] (Eqn [7]) were applied.

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

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

Provided the solid is non-polar, knowledge of its solid surface tension γ_{sv} makes possible the determination the Lifshitz–van der Waals portions of the surface tension[40] (γ_{lv}^{LW}) (Eqn [8]) and solid/liquid interfacial tension[41] (γ_{sl}^{LW}) of any liquid (Eqn [9]).

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

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

The polar portions ($\gamma_{lv}^{+/-}$) and ($\gamma_{sl}^{+/-}$) were calculated in analogy to Fowkes' approach[42] by use of Eqns [10] and [11].

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

$$\gamma_{sl}^{+/-}=\gamma_{sl}-\gamma_{sl}^{LW} \qquad [11]$$

3 RESULTS

3.1 Coating of the glass plate with FC 722®

In order to obtain a finite contact angle in every experiment, the preparation of a plate possessing a solid surface tension $\gamma_{SV} < 15$ mN/m was necessary (surface tension of low-molecular-weight siloxanes[43] ≈ 16 mN/m). After coverage of a solid surface with a perfluoroalkyl methacrylate polymer (FC 721®, 2% by wt polymer solution, solvent fluorochlorohydrocarbon, 3M Corp.) Neumann[44] measured solid surface tensions of about 12 mN/m. For that reason we coated glass plates with FC 722® (identical polymer, solvent perfluoroalkane). Extended experiments showed (Table 4) that strict coating and measuring procedures have to be met to obtain the desired reproducible results.

The preparation and handling modes adopted for the experiments summarized in Table 4 were as follows.

Run I:	one coating cycle; 0.7 mm/s immersion/emersion speed; resting time in the solution 1 min; measurement after 12 h air drying.
Run II:	after run I, four additional coating cycles, with 15 min between the cycles; measurement after 2 h air drying.
Run III:	after run II, extension of the air drying time to 24 h.
Run IV	renewed measurement 1 h after run III.
Run V:	after run IV, cleaning of the plate in n-heptane, 5 h air drying, then measurement.
Run VI:	control measurement at the end of all the experiments with compounds **1** to **28**.

Experiments I and II show that repeated coating cycles strengthen the low-energy character of the coated glass plate (the lower-energy the plate, the lower the force value at a defined immersion depth). An extension of the drying period further strengthens this trend (run III). Experiment IV indicates that despite the low-energy character of the plate and the absence of visible liquid traces, an undesired prewetting (from run III) had taken place. In an attempt to clean the plate and to reduce the time between the experiments, we dipped it several times into n-heptane. After five hours of drying, the immersion curve of run III could be reproduced (run V). In order to control the long-term quality of the coating, we repeated the experiment after the measurements on all the other compounds **1** to **28** (run VI). Minor deviations from run III are within the limits of error.

3.2 Solid surface tension of the coated glass plate

In Section 3.1 we described the preparation of a coating yielding reproducible wetting curves. The solid surface tension of the coating was determined by wetting experiments with a series of n-alkanes. In Table 5 the results are summarized.

Although not investigated in detail, the data for n-pentane seem to be due to the high vapour pressure of the alkane at 20 °C yielding a prewetting (that means a higher-energy modification) of the perfluorinated surface. For this reason the n-pentane results were excluded from further consideration.

The γ_{sv}^{LW} values show a tendency to decrease with increasing chain length of the hydrocarbon. An analogous tendency is not found for the γ_{SV} values. Less pronounced but similar effects have already been described[13] in the course of the characterization of FEP® plates (perfluorinated ethylene–propylene copolymer, γ_{SV} 18.9 mN/m).

The difference in behaviour of γ_{sv}^{LW} and γ_{SV} is due to the treatment of the important interaction parameter Φ in the course of the formulation of the final equations [6] and [7]. van Oss puts $\Phi = 1$ for non-polar hydrocarbons.[45] Neumann introduces a γ_{sl}-dependent Φ.[46] Obviously Neumann's more flexible approach towards the relation γ_{sl}/Φ (Eqn [12]) reflects better the real wetting behaviour of non-polar hydrocarbons on non-

Table 4 Immersion of an FC 722® coated glass plate into liquid **5**

Immersion depth (cm)	*p* (mN/m) Run I	Run II	Run III	Run IV	Run V	Run VI
0.2	0.470	0.460	0.420	0.440	0.420	0.430
0.3	0.450	0.430	0.390	0.410	0.390	0.395
0.4	0.420	0.400	0.370	0.380	0.360	0.370
0.5	0.390	0.370	0.340	0.350	0.340	0.340
0.6	0.360	0.340	0.315	0.320	0.310	0.310
0.7	0.330	0.310	0.290	0.300	0.280	0.280
0.8	0.310	0.285	0.260	0.270	0.255	0.250
0.9	0.280	0.255	0.230	0.240	0.230	0.230

Table 5 Wetting of an FC 722® coated glass plate by n-alkanes and *cis*-decalin

n-Alkane	γ_{lv} (mN/m)	α (mN/m)	γ_{sl} (mN/m)	cos θ	θ (grd)	γ_{sv}^{LW} (mN/m) (van Oss)	γ_{SV} (mN/m) (Neumann)	$\lvert\gamma_{sv}^{LW} - \gamma_{sv}\rvert$
Pentane	16.7	12.5	0	0.748	41.5	12.7	12.8	0.1
Hexane	18.8	11.6	0.9	0.617	51.9	12.3	12.4	0.1
Heptane	20.4	11.4	1.1	0.558	56.1	12.3	12.6	0.3
Octane	21.6	11.0	1.5	0.509	59.4	12.3	12.6	0.3
Nonane	22.9	10.5	2.0	0.458	62.7	12.2	12.6	0.4
Decane	23.8	10.3	2.2	0.432	64.4	12.2	12.7	0.5
Undecane	24.9	9.8	2.7	0.393	66.7	12.1	12.6	0.5
Dodecane	25.4	9.3	3.2	0.366	68.5	12.1	12.7	0.6
Tridecane	26.1	9.3	3.2	0.356	69.2	12.0	12.6	0.6
Tetradecane	26.6	8.6	3.9	0.323	71.2	11.7	12.3	0.6
Pentadecane	27.3	8.5	4.0	0.311	71.8	11.7	12.5	0.8
Hexadecane	27.6	8.2	4.3	0.297	72.7	11.6	12.3	0.7
cis-Decalin	31.8	6.6	5.9	0.201	78.0	11.6	12.7	1.1

polar solids (in a separate paper we will discuss the question whether Eqn [9] is valid for all the substances under investigation).

This result is also in agreement with a chemical understanding of interactions. As it is well known that $-CH_3$ and $-CH_2-$ groups are energetically different,[2] one can expect non-identical interaction parameters Φ for molecules bearing strongly diverging $-CH_3$/$-CH_2$-ratios (n-hexane $-CH_3/-CH_2- = 1:2$, n-hexadecane $-CH_3/-CH_2- = 1:7$). In the case of n-hexadecane the given non-polar solid surface is exposed almost exclusively to the high-energy $-CH_2-$ units with their strong tendency towards interaction between their hydrocarbon chains (crystallization). For the relatively methyl-rich n-hexane, the opposite is true. For increasing differences in the solid surface tenson γ_{sv}/liquid surface tension γ_{lv} ratio this effect is more pronounced.[13] For that reason we determined the solid surface tension of the polymer-covered plate according to Neumann's approach to be 12.5 mN/m.

Nevertheless the good agreement between γ_{SV} and γ_{sv}^{LW} for hydrocarbons of moderate chain length (C_6–C_{12}) proves that the surface is non-polar. A significant donor–acceptor contribution $\gamma_{sv}^{+/-}$ does not exist.

3.3 Surface tensions, wetting tensions and contact angles of various silicon-containing liquids

In Table 6 the results of our measurements on different siloxanes, carbosilanes, polysilanes and silanes are summarized.

4 DISCUSSION

4.1 Surface tension (γ_{lv})

The data in Table 6 demonstrate the striking influence of different backbone bonding types in methylated silicon compounds on the energy balance at the liquid/vapour interface. Wide and flexible bond angles supported by relatively long Si–C bonds (Table 7) enable siloxanes to avoid ordered, intensive and consequently high-energy molecular interactions (see also their boiling points and densities in Table 3).

The exceptional behaviour of the siloxanes becomes clear if one compares silicon- and hydrocarbon-based structures. The incorporation of –O– (donor–acceptor forces) or $-CH_2-$ (Lifshitz–van der Waals forces) moieties into hydrocarbon-based structures yields increasing surface tensions (Table 1); but we also note that the effectivity of the surface tension increase for an –O– incorporation depends on the bond type created.

This well-known rule is only partially valid for silicon-based structures. As expected, additional $-CH_2-$ units between silicon atoms increase the Lifshitz–van der Waals forces and the surface tension (compds **22→15**). In contrast, additional donor–acceptor forces after –O– incorporation are overruled by the dramatic but not well-understood) bond type changes, yielding in this particular case a net reduction in surface tension (compds **22→5**).

The stepwise incorporation of $-CH_2-$ units in the siloxane 'side chains' counterbalances the backbone effect (compds **5→6→9**). Additional

Table 6 Surface tension, wetting tension and contact angle data of compounds **1** to **28**

No.	γ_{lv} (mN/m)	γ_{lv}^{LW} (mN/m)	$\gamma_{lv}^{+/-}$ (mN/m)	γ_{sl} (mN/m)	γ_{sl}^{LW} (mN/m)	$\gamma_{sl}^{+/-}$ (mN/m)	α (mN/m)	cos θ	θ (grd)
Siloxanes									
1	15.2	14.3	0.9	1.0	0.06	0.94	11.5	0.756	40.7
2	15.7	14.6	1.1	1.2	0.08	1.12	11.3	0.719	43.7
3	16.2	15.2	1.0	1.2	0.13	1.07	11.3	0.697	45.5
4	17.0	15.6	1.4	1.6	0.17	1.43	10.9	0.641	49.9
5	16.9	15.3	1.6	1.8	0.14	1.66	10.7	0.633	50.6
6	18.2	17.1	1.1	1.5	0.36	1.14	11.0	0.604	52.7
7	21.8	20.2	1.6	2.5	0.92	1.58	10.0	0.459	62.8
8	17.5	16.2	1.3	1.5	0.23	1.27	11.0	0.628	51.2
9	23.8	21.9	1.9	3.2	1.31	1.89	9.3	0.391	67.0
10	19.0	18.2	0.8	1.4	0.53	0.87	11.1	0.584	54.2
11	18.7	17.9	0.8	1.3	0.48	0.82	11.2	0.599	53.0
Carbosilanes									
12	18.8	17.7	1.1	1.5	0.45	1.05	11.0	0.585	54.3
13	19.1	18.4	0.7	1.3	0.57	0.73	11.2	0.586	53.9
14	21.7	20.6	1.1	2.1	0.90	1.20	10.4	0.479	61.4
15	21.2	19.9	1.3	2.1	0.87	1.23	10.4	0.491	60.6
16	21.2	20	1.2	2.1	0.88	1.22	10.4	0.491	60.6
17	23.0	21.9	1.1	2.4	1.31	1.09	10.1	0.439	64.0
Polysilanes									
18	18.0	17.1	0.9	1.2	0.36	0.84	11.3	0.628	51.3
19	17.9	17.1	0.8	1.2	0.36	0.84	11.3	0.631	50.7
20	18.0	17.3	0.7	1.1	0.39	0.71	11.4	0.633	50.8
21	20.4	18.9	1.5	2.1	0.65	0.45	10.4	0.509	59.4
22	20.5	19.5	1.0	1.7	0.78	0.92	10.8	0.527	58.3
23	20.5	19.3	1.2	1.9	0.73	1.17	10.6	0.517	58.9
24	21.6	19.9	1.7	2.5	0.86	1.64	10.0	0.462	62.5
Silanes									
25	19.2	19.2	0.0	0.7	0.72	− 0.02	11.8	0.615	52.0
26	21.9	21.3	0.6	170	1.16	0.54	10.8	0.493	60.6
Mixed structures									
27	17.8	16.8	1.0	1.3	0.32	0.98	11.2	0.629	51.1
28	19.3	18.6	0.7	1.3	0.60	0.70	11.2	0.580	54.5

Table 7 Bond angles and bond distance of permethylated compounds $(CH_3)_3\mathbf{YXY}(CH_3)_3$

Structure	Angle YXY (°)	Distance X–Y (Å)	Distance Y–CH_3 (Å)	Ref.
$(CH_3)_3\mathbf{SiOSi}(CH_3)_3$	148.8	1.626	1.850	47
$(CH_3)_3\mathbf{SiCH_2Si}(CH_3)_3$	123.2	1.889	1.874	48
$(CH_3)_3\mathbf{SiSi}(CH_3)_3$	—	2.340 (Si–Si)	1.877	49
$(CH_3)_3\mathbf{CCH_2C}(CH_3)_3$	128.0	1.545	1.545	48

dispersion forces, accompanied by a reduction in torsion flexibility,[4] yield increasing surface tensions.

The substitution of $-CH_3$ groups by the smaller H-atoms effects a decrease in surface tension. It is more pronounced for siloxanes than for carbosilanes and polysilanes (compds **3→2→1**; **13→12**; **20→19→18**). Obviously, only siloxanes can use the 'holes' effectively to minimize interactions. Calculations[4] show lower torsion barriers for hydrogen-substituted siloxanes.

The role of the silicon atom in $-Si[(CH_3)_3]$ units becomes clear on viewing the data of the neopentyl-substituted silanes. The substitution of silicon by carbon (compds **12→25**; **16→26**) effects an increase in surface tension. The longer Si–C bonds (see Table 7) yield bulkier trimethylated moieties which inhibit intensive, high-energy interactions.

4.2 Contact angle (θ) and interfacial tension solid/liquid (γ_{sl})

It is one of the major aims of our investigation to compare the contact angle data of a multitude of different low-energy, silicon-containing liquids with those of analogous hydrocarbons.

The data in Tables 5 and 6 show that within the different substance groups (hydrocarbons, siloxanes, carbosilanes, polysilanes, silanes) the contact angles increase with increasing surface tension.

However, this roughly regular behaviour is not valid across group boundaries. Very instuctive for the understanding of the problem are comparisons of the probably most polar and strictly non-polar liquids (siloxanes vs hydrocarbons). Substance **9** and n-decane possess practically the same surface tension but the contact angle differs significantly. The same is true for the pairs siloxane **7**/n-octane and siloxane **10**/n-hexane. In each of these cases the hydrocarbons show the lower contact angles and wet the perfluorinated surface better.

Interestingly, analogous pairs with carbosilanes (compd **12**/n-hexane) and polysilanes (compd **24**/n-octane) can also be established.

These findings for silicon-containing liquids are in line with our results concerning aqueous solutions of carbohydrate-modified silicon surfactants[13] and Zisman's data, adopted by Neumann,[50] for a number of liquids (Table 8). According to these data, the contact angle of a liquid on a given solid is no straight function of the surface tension. The solid/liquid interfacial tension γ_{sl} can be regarded as independent of γ_{lv}. Although including the flexible and useful γ_{sl}/Φ approach, Neumann's 'equation of state' concept finally ignores the point that at the liquid/vapour interface the interactions between the liquid molecules determine the energy balance exclusively (the gas molecules are too diluted), whereas at the solid/liquid interface specific interactions between solid matter and liquid molecules can influence this balance considerably.[13] These specific interactions should be reflected by a γ_{sl} pattern that depends on chemical structure and not on surface tension.

Again, within the substance groups rough correlations between increasing surface tensions γ_{lv} and interfacial tensions γ_{sl} exist. This indicates that for a given structure the force(s) responsible for both interfacial tensions do not change and develop continuously.

Such a correlation is not valid across group boundaries. In the strictly non-polar hydrocarbon series a γ_{sl} value of 1.1 mN/m is reached at 20.4 mN/m surface tension (Table 5, n-octane). Roughly the same data set is obtained for neopentyl-substituted silanes after extrapolation from compounds **25** and **26**. For carbosilanes, 1.1 mN/m solid/liquid interfacial tension is coupled to a surface tension of about 18–19 mN/m.

Table 8 Surface tensions γ_{lv} and contact angles θ of selected liquids on perfluorolauric acid[50]

Liquid	γ_{lv} (mN/m)	θ (grd)
$(CH_3)_3Si[OSi(CH_3)_2]_3OSi(CH_3)_3$	18.1	60
Perfluoroalkane FCD-330	20.2	48
$H(CF_2)_6CH_2OH$	23.8	62
Decane	23.9	70
Di(n-pentyl) ether	24.9	68
$H(CF_2)_2CH_2OH$	27.6	68

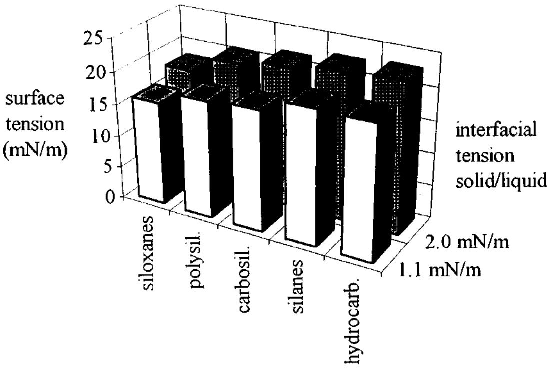


Figure 2

In polysilanes this γ_{sl} value is reached at 18 mN/m (compd **20**). Finally, for non-cyclic methylated siloxanes the values of 1.1 mN/m for γ_{sl} is coupled to about 16 mN/m surface tension (compd. **2**, Table 6, Fig. 2).

Already, from these few examples, it follows that for every single substance group the forces responsible for the liquid vapour and solid/liquid interfacial tensions have to derive from more than one source and occur in different ratios. Not surprisingly the neopentyl-substituted silanes behave as though they are closely related to the hydrocarbons. The substitution of their quaternary carbon atoms by silicon yields the carbosilanes and a first significant deviation. This trend is further strengthened by the complete elimination of carbon from the backbone in polysilanes. Finally, the incorporation of oxygen in the backbone yields molecules possessing completely different energy properties.

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

The major advantage of Neumann's concept, as demonstrated in Section 3.2 for the determination of the solid surface tension, consists in the introduction of a flexible γ_{sl}-dependent interaction parameter Φ (Equation [12].

$$\Phi = -0.0075\gamma_{sl} + 1 \qquad [12]$$

Combination of [12] with the Girifalco/Good approach (Eqn [13]) led to the conclusions that the interfacial tension γ_{sl} (Eqn [14]) as well as the contact angle θ (Eqn [7]) are straight functions of the surface tension γ_{lv} for a given solid (γ_{sv} constant).

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\Phi(\gamma_{sv} \cdot \gamma_{lv})^{0.5} \qquad [13]$$

$$\gamma_{sl} = \frac{(\sqrt{\gamma_{sv}} - \sqrt{\gamma_{lv}})^2}{1 - 0.015\sqrt{\gamma_{sv} \cdot \gamma_{lv}}} \qquad [14]$$

We have already shown in the previous section that these conclusions are not valid for certain types of silicon-containing compounds. Due to the presence of polar oxygen atoms, siloxanes wet the non-polar perfluorinated surface less well than hydrocarbons of the same surface tension. In fact siloxanes behave like the $-CH_2-$ or $-(CH_2)_2-$ chain-extended homologues of those hydrocarbons.

It is an inevitable consequence of Neumann's approach that no possibility is provided for the quantitative description of the sources causing the different behaviour at the liquid/vapour and solid/liquid interfaces.

van Oss *et al.* (Eqn [15]). applying Fowkes' method (Eqn [10]), developed a system based on selective interactions.[38] Φ is put as 1.

$$\gamma_{sl} = (\sqrt{\gamma_{sv}^{LW}} - \sqrt{\gamma_{lv}^{LW}})^2 + 2(\sqrt{\gamma_{sv}^{+} \cdot \gamma_{sv}^{-}} + \sqrt{\gamma_{lv}^{+} \cdot \gamma_{lv}^{-}} - \sqrt{\gamma_{sv}^{+} \cdot \gamma_{lv}^{-}} - \sqrt{\gamma_{sv}^{-} \cdot \gamma_{lv}^{+}} \qquad [15]$$

An approach of this type for a selective treatment of donor–acceptor and Lifshitz–van der Waals interactions is urgently needed to explain the γ_{sl} and contact angle data. Nevertheless we are aware that this quantification of interactions on the present level of understanding is not completely satisfactory. Extended interfacial tension measurements[21] have shown conisiderable differences between experimental data and calculations according to Good's aproach. These deviations probably stem from the inflexible treatment of Φ.[38]

It follows immediately that calculated Lifshitz–van der Waals (γ^{LW}) and donor–acceptor portions ($\gamma^{+/-}$) of surface tension and solid/liquid interfacial tension are no exact measure for the total polarity of an isolated molecule. Instead they reflect the types of interaction preferred by one condensed material in contact with another one.

An inspection of the donor–acceptor portion of the surface tension ($\gamma_{lv}^{+/-}$) shows that siloxanes are the most polar group of substances (Table 6). They are followed by the surprisingly polar carbosilanes[2] and polysilanes. The neopentyl–substituted silanes are closely related to hydrocarbons.

Due to the inceasing polar substructure/methyl group ratio, there is a general trend towards increasing donor–acceptor components within a series of substances.

A detailed analysis of the structure dependence of $\gamma_{lv}^{+/-}$ for the siloxanes discloses the influences of substitutents. The moderately increased surface tension after substitution of a methyl by an ethyl group (compds **5**⟶**6**) is accompanied by a reduced donor–acceptor component. A phenyl substitution (compds **5**⟶**7**) reverses the latter effect. Here the strong surface tension increase is partially due to a renewed $\gamma_{lv}^{+/-}$ increase. Phenyl structures increase both donor–acceptor portions and Lifshitz–van der Waals interactions, whereas ethyl groups strengthen the latter selectively.

We noted for polysilanes, from di- to tetrasilanes, a regular increase of $\gamma_{lv}^{+/-}$. It is an open question whether this trend reflects an increasing acceptor property γ_{lv}^{+} complementary to the known[45] donor capacity γ^{-} of oxygen atoms (Si–O–Si structures) in the case of siliconized glass.

For aqueous solutions of carbohydrate-modified siloxane surfactants on FEP® we found[13] that γ_{sl} and $\gamma_{sl}^{+/-}$ closely follow $\gamma_{lv}^{+/-}$. In a single case a significant Lifshitz–van der Waals component of γ_{sl} was observed.

Due to the very low solid surface tension of the FC 722® coating, this situation could change for the liquid precursors under investigation here. We note that, for every liquid, $\gamma_{lv}^{+/-}$ and $\gamma_{sl}^{+/-}$ practically converge. Obviously, for a given liquid, on both the liquid/vapour and solid/liquid interfaces donor–acceptor forces of the same origin and size occur, but in almost every case we found a considerable γ_{sl}^{LW} component yielding a total γ_{sl} value higher than $\gamma_{sl}^{+/-}$ or $\gamma_{lv}^{+/-}$. Although rich in methyl groups, and in the case of siloxanes very flexible, the liquids tested cannot completely compensate the dispersion forces emerging on this perfluorinated surface. In Sections 4.2 we discussed in detail the fact that liquids of the same surface tension do not necessarily produce the same contact angle on a given solid. The correlation of the donor–acceptor and Lifshitz–van der Waals components of the surface tension γ_{lv} and the solid/liquid interfacial tension γ_{sl} with structural aspects helps decisively to improve the understanding of this phenomenon.

For the phenylated siloxane (**7**) and the neopentyl substituted silane (**26**) almost identical surface tensions have been measured. Due to the presence of electron-donating oxygen atoms and the aromatic ring, the siloxane possesses a higher $\gamma_{lv}^{+/-}$ and a diminished γ_{lv}^{LW} component. Obviously a given surface tension can be the result of the superposition of different types of force in different proportions. In contact with non-polar, condensed matter at the solid/liquid interface the liquids do not behave in an identical way any longer. For the siloxane a considerably higher γ_{sl} value was found. Furthermore, this total γ_{sl} value mainly stems from a donor–acceptor component ($\gamma_{sl}^{LW}/\gamma_{sl}^{+/-} \approx 0.6:1$). The lower γ_{sl} value for the neopentyl-substituted silane predominantly derives from Lifshitz–van der Waals forces ($\gamma_{sl}^{LW}/\gamma_{sl}^{+/-} \approx 2.1:1$). The difference between the two compounds essentially arises from the point that existing donor–acceptor forces exhibit the same strengths at both interfaces (compd **7**: $\gamma_{lv}^{+/-}$ 1.6 mN/m$\longrightarrow\gamma_{sl}^{+/-}$ 1.6 mN/m) where Lifshitz–van der Waals forces occur in strikingly different magnitudes (compd **7**: γ_{lv}^{LW} 20.2 mN/m$\longrightarrow\gamma_{sl}^{LW}$ 0.9 mN/m).

From this it becomes clear why the proposition ‘identical surface tensions—identical contact angles’ is still disputed. Contact angle differences for a given surface tension on a defined solid (γ_{SV} constant) have to derive from γ_{sl} differences. But the considerable differences determined for γ_{lv}^{LW} (between compds **7** and **25** $\Delta\gamma_{lv}^{LW}=1.1$ mN/m) are accompanied by minor γ_{sl}^{LW} differences ($\Delta\gamma_{sl}^{LW}=0.3$ mN/m). Exclusively the donor–acceptor difference is effective ($\Delta\gamma_{lv}^{+/-}=1.0$ mN/m, $\Delta_{sl}^{+/-}=1.1$ mN/m). Because of the small absolute value of $\Delta\gamma_{sl}$ compared with γ_{lv} and γ_{sv} (in each case identical for the substance pair under investigation) in the Young equation (Eqn [1]), minor contact angle differences result.

It emphasizes the value of the Wilhelmy-based multipoint wetting measurements that, after an intensive calibration procedure, these differencs can be detected accurately.

Acknowledgements The research project ‘Siloxanyl-modified Carbohydrates’ was financially supported by the German Ministry for Research and Technology (Reg. No. 0310317 A/B). The project ‘Polyhydroxylated Silicon Compounds’ is supported by the Deutsche Forschungsgemeinschaft (Reg. No. WA 1043/1-1).

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