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Silicon-Modified Carbohydrate Surfactants VIII. Equilibrium Wetting of Perfluorinated Solid Surfaces by Solutions of Surfactants Above and Below the Critical Micelle Concentration—Surfactant Distribution Between Liquid–vapour and Solid–liquid Interfaces

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For selected carbohydrate-modified Silicon surfactants of the siloxane, carbosilane, polysilane and silane type, the concentration dependences of the liquid/vapour and solid/liquid interfacial tensions under equilibrium conditions have been determined. Further, the Lifshitz–van der Waals and donor–acceptor contributions have been calculated. Below the critical micelle concentration (cmc) a steep increase in donor–acceptor contributions to both interfacial tensions was found. The Lifshitz–van der Waals contribution of the liquid/vapour interfacial tension shows a pronounced minimum. Calculations of the concentration-dependent surface coverage suggest that preferential adsorption to one of the interfaces does not take place. Copyright © 1999 John Wiley & Sons, Ltd.

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1 INTRODUCTION

Aqueous solutions of certain trisiloxane surfactants rapidly wet low-energy surfaces[1] (i.e. polyethylene, polypropylene, layers of natural waxes), but commercially available 'superspreaders' (e.g. Silwet L77, Union Carbide) usually consist of complex mixtures bearing species with four to 12 ethylene oxide units attached to a trisiloxane moiety. So far the question of the active species within these mixtures has been unsolved.

Chemical, geometrical, kinetic and energetic influences have been found to govern this superspreading process.[1–5] Although liquid/liquid interfacial tension measurements cannot simulate the situation at the solid/liquid interface (smoothness of an oil phase, partial surfactant solubility in it), the first dynamic data for the aqueous silicon surfactant solution–n-alkanes system[6] suggest that bulk diffusion coefficients of superspreaders are one order of magnitude higher than those of conventional surfactants. Nevertheless a clear-cut quantification of the energetic situation during the fast-progressing wetting of a solid material by a surfactant solution remains a challenging task.

Within the framework of a comprehensive investigation of the wetting behaviour of silicon surfactants we synthesized strictly defined silicon-modified carbohydrate surfactants of the siloxane, carbosilane, polysilane and silane types.[7–9] We were able to quantify the impacts of substructures (silicon moiety, spacer, carbohydrate unit, modifying element) on the equilibrium wetting behaviour

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of diluted aqueous surfactant solutions on perfluorinated solid surfaces.[10,11] In order to ensure the significance of the underlying trends and the comparability with corresponding data of liquid silicon precursors[9,12] we had to focus our attention on surfactant solutions above the critical micelle concentration (cmc). It could be demonstrated that the liquid/vapour (γ_{lv}) and solid/liquid (γ_{sl}) interfacial tensions develop independently. Above the cmc, Lifshitz–van der Waals contributions dominate the energetic balance at the liquid–vapour interface, whereas a structure-dependent sensitive equilibrium between Lifshitz–van der Waals (LW) and donor–acceptor (+/−) contributions exists at the solid–liquid interface. The existence of fundamentally diverging energetic situations at the different interfaces in one system immediately leads to the widespread problem of emulsion stability. Apart from well-understood thermodynamically stable microemulsions,[13,14] the preparation of conventional metastable emulsions has remained a field of empirical experience. Concentrates which are diluted before application by at least two orders of magnitude are especially difficult to handle and tend to break. Few attempts have been made[15,16] to correlate emulsion stability and energetic data.

Therefore it is the purpose of this paper to investigate the concentration dependences of γ_{lv} and γ_{sl} as well as their Lifshitz–van der Waals and donor–acceptor contributions. Further, we investigated the question of where surfactant molecules are adsorbed in the case of competing surfaces (below the cmc).

2 MATERIALS AND METHODS

2.1 Materials

Eleven defined silicon surfactants bearing one carbohydrate moiety (Fig. 1) and one derivative bearing two carbohydrate units (Fig. 2) were chosen for the equilibrium wetting experiments. Structurally they belong to the class of amides of O^5-α-D-glucopyranosyl-D-arabinonic acid. Their synthesis and chemical characterization have been described earlier.

2.2 Methods

At equilibrium the macroscopic behaviour of a liquid on a plane solid surface is determined by three forces: (i) liquid/vapour interfacial tension

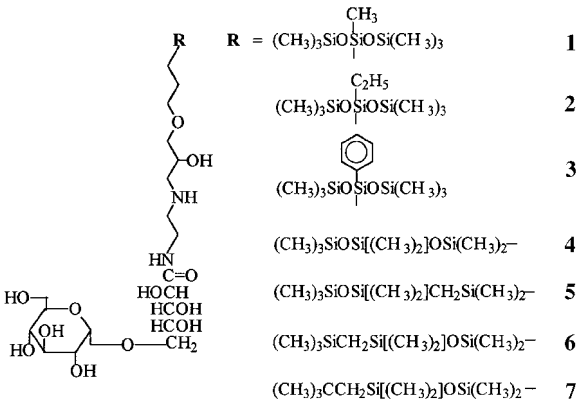

Figure 1 Structures of the carbohydrate-modified silicon surfactants **1–11.**

(surface tension of the liquid γ_{lv} or σ); (ii) solid/vapour interfacial tension (solid surface tension $_{sv}$); and (iii) solid/liquid interfacial tension (γ_{sl}) (Fig. 3; Young's equation,[17] Eqn [1]):

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

where α = wetting tension.

Therefore the equilibrium contact angles of aqueous surfactant solutions can be determined by measuring independently the liquid/vapour interfacial tension γ_{lv} (σ, ring method, data corrected according to Harkins and Jordan[18]) and the wetting

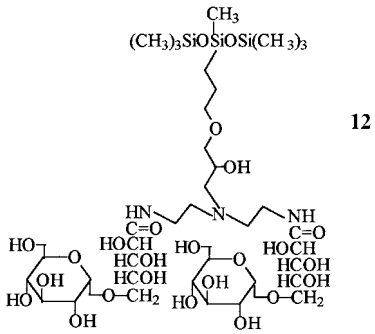

Figure 2 Structure of the carbohydrate-modified silicon surfactant **12.**

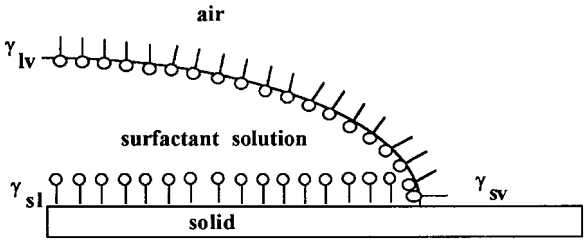

Figure 3 Drop of a surfactant solution on a plane solid.

tension α (Wilhelmy method). The measurements are carried out at 20°C.

To measure accurately the wetting tension α an FEP® plate (tetrafluoroethylene–hexafluoropropylene copolymer, Du Pont) of defined width and thickness is dipped stepwise (2 mm per step, usually 10–15 steps) into a surfactant solution of known concentration with an accuracy of 0.01 mm (Fig. 4). The force (p) measured correlates to α according to Eqn [2]:

$$p = u\alpha - \rho g d b x_i \qquad [2]$$

where

u = perimeter of the FEP® plate
ρ = liquid density
g = gravitational constant
m = mass of the liquid in the meniscus
d = thickness of the plate
b = width of the plate
x_i = immersion-depth of the plate.

After every movement of the plate we measured the force immediately and after 5 min. This time was found to be necessary for the system to reach a force equilibrium between the wetting-tension-induced advance of the meniscus and the meniscus

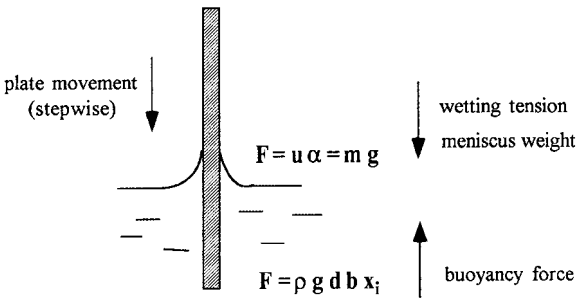

Figure 4 Force balance at an FEP® plate under equilibrium conditions.

weight. In this equilibrium state the meniscus of the surfactant solution does not advance or recede any more and the measured force remains constant. By plotting the 5-min values of the force p against the immersion depth x_i, the product of wetting tension α and perimeter u is obtained by extrapolation to $x_i = 0$.

In order to determine the concentration dependence of surface tension γ_{lv} and wetting tension α, the above general procedure was repeated for diluted surfactant solutions in the range 10^{-2}–10^{-7} mol l^{-1}.

The interfacial tension γ_{sl} can be calculated from the γ_{sv}–α relationship (see Eqn [1]).

The procedure for the separate determination of the solid/vapour surface tension γ_{sv} of FEP® has been described earlier.[10] The fact that FEP® is strictly non-polar eliminates a complicating donor–acceptor term $\gamma_{sv}^{+/-}$ from the calculations. A strictly Lifshitz–van der Waals-force-based solid/vapour interfacial tension $\gamma_{sv} = \gamma_{sv}^{LW} = 18.9$ $mN^{-1}m$ has been used for all calculations. Therefore we were able to determine in a simple way the Lifshitz–van der Waals contributions. γ_{lv}^{LW19} (Eqn [3]) and γ_{sl}^{LW20} (Eqn [4]).

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

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

The donor–acceptor portions ($\gamma_{lv}^{+/-}$) and ($\gamma_{sl}^{+/-}$) were calculated according to Fowkes' approach[21] (Eqn [5]):

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{+/-} \qquad [5]$$

Since below the cmc the number of surfactant molecules in a given system is not sufficient to establish a maximum coverage of all interfaces we determined the distribution of the surfactant molecules between the liquid–vapour and solid–liquid interfaces.

The coefficients

$$\frac{d\gamma_{lv}}{d(\log / c_{bulk})} \quad \text{and} \quad \frac{d\gamma_{sl}}{d(\log / c_{bulk})}$$

can be determined for defined bulk concentrations from the corresponding γ_{lv}–ln c and γ_{sl}–ln c isotherms and put into the Gibbs equation[22] (Eqn [6]), which describes the relation between a given

bulk concentration (c_{bulk}) of a surfactant, its interfacial excess (Γ_c) and a measured interfacial tension (γ_i):

$$\Gamma_c = \frac{-1}{RT}\left(\frac{d\gamma_i}{d(\ln c_{bulk})}\right) = \frac{-1}{2.302RT}\left(\frac{d\gamma_i}{d(\log c_{bulk})}\right) \quad [6]$$

The area per surfactant molecule (A) at a given bulk concentration can be determined from Eqn [7]:

$$A = \frac{1}{N\Gamma_c} \quad [7]$$

where N = Avogadro's number = 6.02×10^{23} mol^{-1}.

3 RESULTS

For selected compounds the data concerning the concentration dependence of the liquid/vapour (γ_{lv}) and solid/liquid (γ_{sl}) interfacial tensions, their Lifshitz–van der Waals (γ_{lv}^{LW}, γ_{sl}^{LW} and corresponding donor–acceptor ($\gamma_{lv}^{+/-}$, $\gamma_{sl}^{+/-}$) contributions are summarized in Fig. 5, which shows that both interfacial tensions start to increase below the same concentration (cmc). The steep increase in γ_{sl} is exclusively attributable to an increase in the donor–acceptor contribution $\gamma_{sl}^{+/-}$. The corresponding Lifshitz–van der Waals contribution does not play a significant role. Since both donor–acceptor contributions are of the same size, a general pattern $\gamma_{sl} \approx \gamma_{sl}^{+/-} = \gamma_{lv}^{LW}$ is found. For every surfactant under investigation we found a minimum of γ_{lv}^{LW} in the concentration range characterized by the steepest increase in γ_{lv}.

The coverage of the solid–liquid and liquid–vapour interfaces with surfactant molecules is depicted in Fig. 6 The area occupied by one molecule decreases with increasing concentration. The frequently detectable minor preference for the liquid/vapour interface falls within the error limits.

4 DISCUSSION

The wetting behaviour of pure liquids on solid surfaces has been investigated extensively.[23,24] For completely miscible two-component systems meaningful results cannot be expected yet, however.[25] Probably, therefore, only a few systematic attempts have been made to determine the surfactant concentration dependence of the poorly accessible solid/liquid interfacial tension. Yaminsky[26] found for a negatively charged mica surface in contact with a cationic surfactant solution an adsorption preference for the liquid–vapour interface at low concentrations. Wolfram[27] investigated the PTFE–sodium dodecylsulphate solution system and found an increase in the wetting tension α with increasing surfactant concentration. The contact angle decreases and reaches an equilibrium value above the cmc. Chaudhury[28] studied the adsorption of aqueous solutions of heptaethyleneglycol monododecyl ether on a modified PDMS surface. At surface saturation the solid–liquid interface was found to be slightly less densely covered with surfactant molecules than the liquid–vapour one.

The few available data cannot answer the following apparently simple questions:

(1) Do the ratios of the corresponding Lifshitz–van der Waals and donor–acceptor contributions of the liquid/vapour (γ_{lv}) and solid/liquid (γ_{sl}) interfacial tensions change if one dilutes relatively concentrated surfactant solutions from above the cmc to water-like systems?
(2) Does the surfactant structure (i.e. the presence of silicon moieties) have a significant influence on these possible changes?
(3) Where are the surfactants adsorbed if both interfaces have to compete for molecules below the cmc?

First, we found in all cases (Fig. 5) a cmc(γ_{sl}) close to the cmc(γ_{lv}).[28] Obviously a state of complete surface coverage under equilibrium conditions is bound to a single well-defined bulk concentration.

Since this finding does not allow predictions on the situation below the cmc we used the Gibbs equation (Eqn [6]) to calculate the concentration-dependent surface coverages. We are aware that interfacial-energy-mediated surface coverage calculations using the slopes of the logarithmically scaled isotherms involve a considerable error (estimated error 50%). But since the development of direct methods relating given bulk concentrations and the corresponding interfacial concentrations is still at its very beginning,[29] no alternative measurement principle could be applied. Instead, we analysed the isotherms of a broad spectrum of substances to validate the results.

From the surface coverage data (of which there are selected examples in Fig. 5), no pronounced

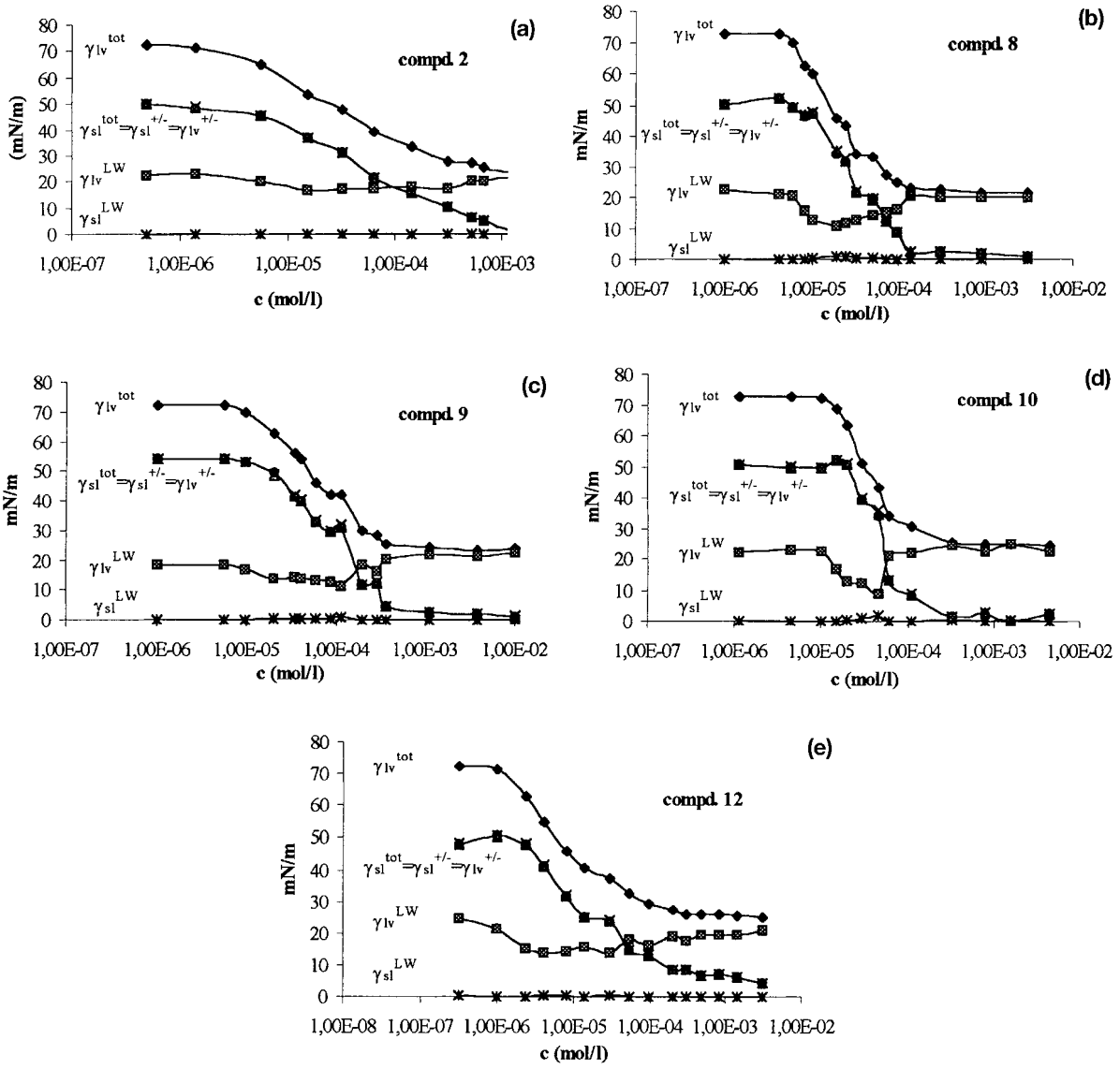

Figure 5 Liquid/vapour and solid/liquid (tot) interfacial tensions on FEP® donor-acceptor (+/−) and Lifshitz–van der Waals (LW) contributions are also shown.

preferential adsorption takes place below the cmc. A given bulk concentration yields roughly comparable interfacial concentrations. We are somewhat surprised to observe that neither the type of the hydrophobic moiety (e.g. compound **8** is a typical siloxane; compound **10** is practically hydrocarbon-like) nor a change in the molecular geometry (e.g. incorporation of a second hydrophilic carbohydrate unit in **12**) alters this general trend. Unfortunately the frequently detectable slight preference for the liquid–vapour interface falls within the error limits.

These results for the solutions of non-ionic silicon surfactants in contact with a non-polar surface deviate from that obtained for the charge-determined mica–cationic surfactant system.[26] This achieves immediate practical importance because it can help to understand one aspect of the well-known phenomenon of emulsion concentrate instability during dilution. A stable emulsification of a relatively non-polar substance depends on a sufficiently dense surfactant layer at the solvent (i.e. water)–substance interface. Dilution of a

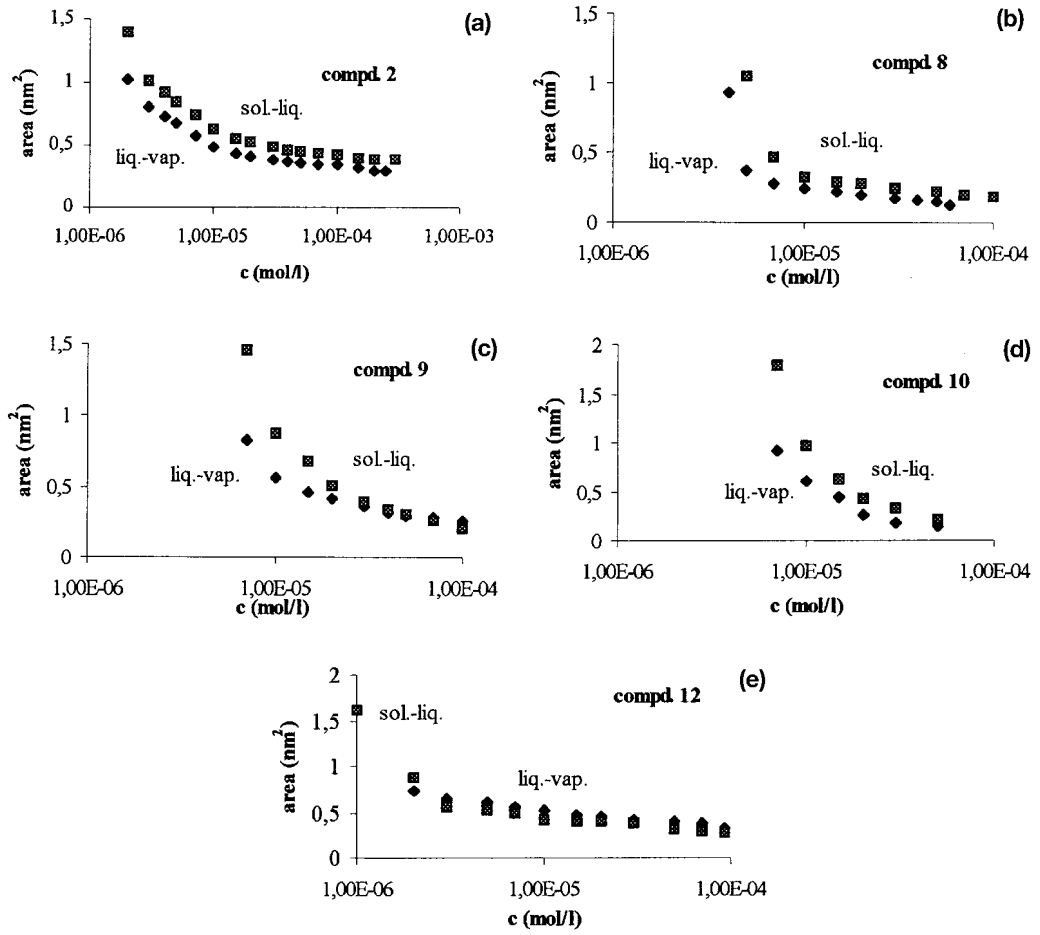

Figure 6 Concentration dependence of the area per surfactant molecule at the liquid/vapour and solid/liquid interfaces.

concentrate of the substance by typically two or three orders of magnitude in water (that means a shift to much lower equilibrium bulk concentrations of the surfactant) can cause an even desorption of surfactant molecules from the water–vapour and substance–water interfaces. The system becomes unstable.

A large-scale desorption of surfactant molecules is accompanied by an increased appearance of water at the interfaces (and probably also by a change in orientation of the remaining surfactant molecules[28]). The energetic consequences must be dramatic because an analysis of the surface tension data of donor–acceptor-force-determined water, and a Lifshitz–van der Waals-force-determined pure oxyalkylene-modified trisiloxane surfactant, has already disclosed major differences (Table 1).

Figure 5 proves that major energy changes take place after dilution below the cmc. The structure of the silicon surfactant plays a minor role. The shapes of the γ_{lv}–log c and γ_{sl}–log c curves are similar; they both increase steeply below the cmc.[27,28] Of principal importance for an understanding of the superspreading process and the emulsion stability phenomenon in general is the analysis of the Lifshitz–van der Waals and donor–acceptor contributions of both interfacial tensions.

Table 1 Surface tensions (γ_{lv}), Lifshitz–van der Waals (γ_{lv}^{LW}) and donor acceptor ($\gamma_{lv}^{+/-}$) contributions of water[23] and Silwet L77[9] {$[(CH_3)_3SiO]_2CH_3Si(CH_2)_3(OCH_2CH_2)_{7.5}OCH_3$}

	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})
Water	72.8	21.8	51
Silwet L77	24.6	20.8	3.8

Table 2 Concentration-dependent minima of γ_{lv}^{LW}

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
$c\ 10^{-5}$ (mol/l^{-1})	4.4	1.5	2.7	3.7	5.1	2.4	1.2	1.9	11	4.5	2.3	3.0
γ_{lv}^{LW} (mN m^{-1})	9.2	17	16.6	11.3	16.2	17.5	15.4	10.9	11.2	8.9	16.2	13.7

It was stated earlier[10,11] that above the cmc γ_{lv} is determined by Lifshitz–van der Waals contributions, whereas for the (much smaller) γ_{sl}, a structure-dependent balance between Lifshitz–van der Waals and donor–acceptor contributions exists. Below the cmc the situation changes considerably. The $\gamma_{lv}^{+/-}$ and $\gamma_{sl}^{+/-}$ contributions are identical and increase steeply with decreasing surfactant concentration, whereas γ_{lv}^{LW} shows a significant minimum just within the concentration range characterized by the steepest γ_{lv} increase. γ_{sl}^{LW} remains too small to evaluate its possible change.

A concentration shift below the cmc not only changes the interfacial energies in a quantitative sense but, probably more importantly, their qualitative composition. In general, diluted surfactant solutions are progressively determined by donor–acceptor forces. Due to the occurrence of water at the liquid–vapour interface, $\gamma_{lv}^{+/-}$ exceeds γ_{lv}^{LW} below the cmc. The much smaller, and above the cmc in its composition surfactant structure dependent γ_{sl}[11], upon dilution converts to a donor–acceptor force determined interfacial energy (below cmc $\gamma_{sl} \approx \gamma_{sl}^{+/-} = \gamma_{LV}^{+/-}$).

We were somewhat surprised to find, for every surfactant, a minimum of γ_{lv}^{LW} (Table 2). Typically, γ_{lv}^{LW} values range from 19 to 24 mN m^{-1} for silicon surfactant solutions above the cmc. The corresponding value for water (see Table 1) is 22 mN m^{-1}. Therefore the γ_{lv}^{LW} minimum does not reflect a single-component property but should be due to a surface structuring effect.

Since no meaningful correlation between the chemical structure of the surfactant and the depth of the minimum was found, its nature remains uncertain. We assume that in a situation where neither water nor the surfactant molecules can establish their specific surface structure, such deviations can occur. The problem may be superposed by concentration-dependent different orientations of the surfactant molecules.[28–30]

We discussed the question of emulsion stability below the cmc in terms of a surfactant depletion at the interfaces. An inspection of the Lifshitz–van der Waals and donor–acceptor contributions of both interfacial energies immediately discloses a second impact. A predominantly non-polar substance cannot interact with forces of the donor–acceptor type created by increasing amounts of water at the interfaces. A decreased stability is the consequence.

The same argument could be important for an understanding of the superspreading process. If at the very edge of a spreading drop, the density of the surfactant molecules decreases temporarily, considerable $\gamma_{lv}^{+/-}$ and $\gamma_{sl}^{+/-}$ contributions emerge. The spreading condition $\theta = 0°$ is not fulfilled until new surfactant molecules fill the 'gaps' and reduce the donor–acceptor contributions locally.

Conclusive evidence for the role of the interfacial energies and their different contributions during a spreading process can provide energetically controlled dynamic wetting experiments which will be discussed in a companion paper.[31]

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