180. Chemically Modified Silicon Dioxide Surfaces

Wetting Properties of Compact n-Alkyl-dimethylsiloxy Layers, and their Mixed Surface Crystals. The Question of Wetting of Molecularly Rough and of Swollen Surfaces

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In Memoriam Prof. *Heinrich Labhart*

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Summary

By means of contact angle measurements, it has been shown that compact alkyl-dimethyl-siloxy layers can be obtained on the surface of acid leached glass using the method previously developed for fume silica. Subsequently, a series of densest possible alkyl-dimethylsiloxy layers were prepared having non-branched alkyl substituents, C_zH_{2z+1}, (with z= 1, 2, 3, 6, 10, 14, 18 and 22) and wetting angles were measured as a function of the temperature. On surfaces coated with longer alkyl substituents the formation of mixed crystals, consisting of the sparse chemically bonded alkyl layer and a n-alkane acting as a wetting agent, has been observed at low temperatures. At higher temperatures such surfaces appeared to be 'molten', and at the same time swollen by the wetting agent. Equations have been derived to deduce the free surface energies and to account for the wetting properties of rough and swollen surfaces. Application of the results to the data presented in this paper revealed that glass surfaces covered with short alkyl chains (methyl, ethyl and propyl) are rough and those covered with long chains (tetradecyl, octadecyl and docosyl) are swollen. Surfaces formed by hexyl- and decyl-dimethylsiloxy substituents exhibit intermediate properties.

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1. Introduction. - Chemically bonded organic layers, exposing long alkyl substituents on the surface of silicon dioxide exhibit two interesting features. On the one hand, they can be considered as 'chemically bonded solvents', and are actually used as such in liquid chromatography. On the other hand, such layers also possess the characteristics of a surface. In the present paper, their wettability is studied. This can certainly be expected to involve complex phenomena, since a wetting agent can swell the 'bonded solvent'. Thus, with every different agent used, a new, mixed surface layer is formed. However, for purposes of study, bonded layers also have definite advantages over physically adsorbed films. In the first place, they do not desorb during wetting experiments, and are insoluble in the wetting agent. In the second place, much valuable information is available about the non-wetted surface from the study of their synthesis. Such an approach, *i.e.* the combination of information, deduced both from chemical synthesis and from contact angle measurements, is certainly not new; but neither is it a fully explored possibility for aiding the understanding of surface phenomena.

On the basis of simple stereochemical considerations a model has been proposed for unwetted surfaces covered by R-dimethylsiloxy groups, where R stands for an n-alkyl substituent, C_zH_{2z+1} (z = 1, 2, 3, 6, 10, 14, 18 or 22) [1]. It has been shown that the hydrated surface of fume silica can be coated with a compact layer, the surface concentration of which is determined by the size of the base of the substituent *(Fig. 1)*. Strictly speaking, the most dense layer is formed only by the methylene-dimethylsilyl part of the substituent. The alkyl chains will lie, one upon the other, in a more or less disordered fashion, producing a sparser 'heather' in the upper layer. The densest layer was prepared by reacting the surface hydroxyls with R-dimethylsilanol at 100 °C in three consecutive treatments using ammonia as catalyst. This resulted in a surface concentration of 4.7 $\mu mol\, m^{-2}$ for methyl, and 4.1 $\mu mol\, m^{-2}$ for longer-than-decyl substituents. In comparison, the concentration of compressed monolayers of alkyl derivatives with small polar groups (carboxylic acids, amines, alcohols *etc.*) on the surface of water, is of the order of $\Gamma_{alkyl} = 7.6\text{-}8.3\ \mu mol\, m^{-2}$ [2] [3].

The thickness of the swollen layer is easily estimated by supposing that the alkyl substituents are now arranged, in the extended configuration, as 'brushes'.

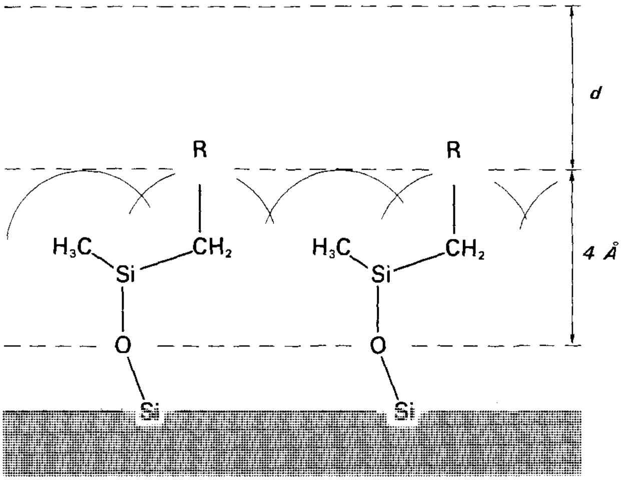

Fig. 1. *Schematic representation of the bonded alkyl-dimethylsiloxy layer on the surface of silicon dioxide.* Bond angles and distances are approximately to scale, assuming a surface concentration of 4.1 $\mu molm^{-2}$. For longer alkyl chains, the thickness, d, is given by Eq. (1) and (2). Note that the second methyl group is not visible in the projection chosen, as it is covered by the first methyl substituent.

Taking the surface of the supposedly impenetrable methylene-dimethylsiloxy layer as base *(Fig. 1)*, the length of the C–C bond as 1.54 Å and assuming tetrahedral angles between carbon atoms, one obtains for a n-alkyl substituent

$$d_{max} = 1.26 \times (z-1)\,\text{Å}. \tag{1}$$

The thickness of the dry layer of longer alkyl chains can be roughly estimated by comparing the packing of alkyl chains in a dense layer on a water surface ($\Gamma_{alkyl} = 7.6\text{–}8.3\ \mu\text{mol}\,\text{m}^{-2}$) or in crystalline polyethylene [4] ($9.1\ \mu\text{mol}\,\text{m}^{-2}$) with that on the surface ($4.1\ \mu\text{mol}\,\text{m}^{-2}$). The latter figure is only about half of that in dense arrangements so that

$$d_{min} \approx 0.5\ d_{max}. \tag{2}$$

The synthetic study resulted also in a method of synthesis for the preparation of layers of maximum surface concentration on hydrated fume silica. This material, although excellent for carrying out and checking synthetic work, is not convenient for the study of contact angles. Therefore, the question was posed as to whether, by the same method, the densest layers could also be prepared on the quartz like [5] surface of acid leached glass. The results are summarized in 2.1, and although they do not constitute proof, they do suggest that this is very probably the case. Therefore, wetting angles were determined in such glass capillaries. The results of a systematic study on n-alkanes on n-alkyl covered surfaces is described in 2.3. Finally, in 2.4 a semi-theoretical treatment is presented for the relationship between contact angles on rough and swollen solids. The theoretical results are used to interpret the wetting experiments.

2. Results and discussion. - 2.1. *Analogies between the synthesis of alkyl-dimethylsiloxy layers on fume silica and on acid-leached glass.* On fume silica after one treatment with alkyl-dimethylsilanol, without a catalyst, the surface concentration of alkyl-dimethylsiloxy groups, $\Gamma_{siloxy} = 3.1\ \mu\text{mol}\,\text{m}^{-2}$, was independent of the length of the non-branched alkyl substituent in the alkyl-dimethylsilanol, and of the temperature of the reaction, over the range 200–350 °C [1]. It was concluded, therefore, that this limiting concentration is determined by the geometry of the underlying surface of amorphous silica. On the other hand, the surface concentration of densest layers, prepared by three successive treatments did depend on the temperature and slightly but definitely on the chain length. The temperature dependence could be deduced from the general rule that the quadratic coefficient of thermal expansion for organic matter is about 0.00067 degree^{-1} giving

$$\Gamma_{siloxy}(T) = \Gamma_{siloxy}(T^{\dagger}) \exp[-0.00067(T-T^{\dagger})] \tag{3}$$

where T is the temperature of the three successive treatments and $T^{\dagger} = 100\ °C$, the temperature at which the densest layer was obtained.

Eq. (3) was in excellent agreement with observation within the range: 100° to 250 °C [1].

By analogy, it was expected, that on leached and hydrated glass surfaces after one treatment without a catalyst, the surface geometry would again be the determining factor. As there is no good model for such surfaces, it was not possible to predict the surface concentration. It was foreseen only that it should be lower after one than after three treatments. On the other hand, it was expected that after three treatments, with or without an ammonia catalyst, the densest layer would be formed at the same concentration as that on fume silica.

From Eq. (3) it was calculated that 90% coverage will be obtained at 258 °C. Three different sorts of capillaries were therefore prepared: type A was treated once at 250 °C, and supposedly having a lower surface concentration than type B capillaries treated three times at the same temperature. Finally, capillaries type C, having the maximum surface concentration, were treated three successive times at 100 °C. Treatments at 250 °C were carried out without a catalyst, at 100 °C with an ammonia catalyst.

If there is an analogy between the synthesis on fume silica and acid leached glass, the surface should be progressively more covered in the order $A(\Gamma_A = ?) < B(\Gamma_B = 90\%) < C(\Gamma_C = 100\%)$. Consequently the surface energy should diminish and contact angles should be highest for capillary C.

In *Table 1* the average decrease of the cosine of the wetting angle is summarized, for capillaries type A and type B. Four groups of wetting agents were used: paraffins, cyclic hydrocarbons, aromatic hydrocarbons and halogenobenzenes; and four different surfaces: methyl-, propyl-, hexyl- and octadecyldimethylsiloxy groups. Two main effects are observed. Firstly, the decrease is most pronounced for the trimethylsiloxysurface and diminishes gradually with increasing length of the alkyl substituent. Secondly, the change in wetting angles is more pronounced with more polarizable and/or polar wetting agents. The overall effect is the expected lower wettability of the repeatedly treated surface.

Layers prepared at 100 °C should be even denser. In *Figure 2* cosines of wetting angles of n-paraffins are shown for the four surfaces corresponding to the four different substituents, each prepared by method B (filled circles) and C (open

Table 1. *Change of the average of cosine of contact angles on surfaces modified by alkyl-dimethylsiloxy groups after three successive treatments of acid leached glass surfaces* (capillary B) *compared with surfaces after one treatment* (capillary A). $\delta = \cos\bar{\theta}_B - \cos\bar{\theta}_A$ at 20 °C. For individual values and further details see *Table 5*.
N: number of substances in the group.

Substance type	N	Surface covered with R-dimethylsiloxy				Average over all surfaces
		methyl	propyl	hexyl	octadecyl	
Paraffins C_xH_{2x+2}	10	−0.014	−0.006	+0.001	+0.003	−0.004
Cyclic hydrocarbons	2	−0.001	−0.006	−0.008	−0.001	−0.004
Aromatic hydrocarbons	4	−0.027	−0.018	−0.011	−0.004	−0.015
Halogenobenzenes	4	−0.045	−0.004	−0.012	+0.002	−0.015
Average over all substances	20	−0.022	−0.009	−0.008	+0.000	

circles). In summary, the overall effect is the expected lower wettability in the order A>B>C, being lowest on the surface layer prepared at 100°C. The effect of the difference in surface concentration of the substituents between B and C is more pronounced on surfaces with longer chains, and opposite to differences between A and B.

Having demonstrated the analogy between the density of the layers on fume silica and on acid-leached glass surfaces a final check was made on the homogeneity of these layers, believed to be the densest. On heterogeneous surfaces, there is a hysteresis between advancing and receding wetting angles. Glass surfaces were therefore coated with different substituents, using method C. As shown in *Table 2* they show only a very slight hysteresis, suggestive of a quite homogeneous surface.

Table 2. *Average cosine of advancing* (a) *and receding* (r) *contact angles of n-paraffins* (nonane to hexadecane) *on surfaces covered with the densest R-dimethylsiloxy layers.* Treatment: 100°C/ammonia as catalyst/8 hrs/three successive treatments. Measurements at 20°C. For individual values, see *Table 6.*

	R							
	methyl	ethyl	propyl	hexyl	decyl	tetradecyl	octadecyl	docosyl
a	0.8401	0.9229	0.9303	0.9429	0.9528	0.9386	0.8581	0.8829
r	0.8414	0.9255	0.9316	0.9439	0.9536	0.9385	0.8616	0.8868
r−a	+0.0013	+0.0026	+0.0013	+0.0010	+0.0008	−0.0001	+0.0035	+0.0039

2.2. *General wetting behaviour of the alkyl-dimethylsiloxy layers.* In *Figure 2* the cosines of wetting angles are plotted as a function of the surface tension of the wetting agent on methyl-, propyl-, hexyl- and octadecyl-dimethylsiloxy-surfaces. On each surface the points fall into two distinct categories: n-paraffins form one class, polarizable and polar substances the other. The branched paraffin, squalane, is in the first class for methyl- and in the second for octadecyl-dimethylsiloxy surface.

The trimethylsiloxy surface is better wetted by polarizable and polar compounds. It must be supposed therefore that the dipolar surface shielded only by a thin layer of the methyl groups, attracts this class of molecules not only via dispersion forces [6] but, following the idea of *Zettlemoyer* [7], also by polar interactions. Paraffins can interact only by dispersion forces so the 'critical surface tension' of the surface, given by the intersection of the lines with the horizontal at $\cos\theta = 1$, [8] [9], is lower when measured for this class of compounds.

For longer substituents (hexyl) the solvent can interpenetrate the alkyl layer. The underlying dipole layer becomes more and more shielded, and consequently, the difference between the two classes of compounds disappears. Finally for the octadecyl-dimethylsiloxy surface the results for all the compounds appear to be scattered around the same regression line, but the n-paraffins show anomalous behaviour. The line has a smaller slope than that for the hexyl-dimethyl-surface but intersect the horizontal at $\cos\theta = 1$ at the same point *(Fig. 2a).* This suggests that the octadecyl layer is 'swollen' by the wetting agent, and that a new mixed surface is formed which determines the contact angle. On the other hand, this relatively thick layer completely shields the underlying dipoles, so that there is no difference in behaviour between squalane and the polar compounds.

The wetting of the octadecyl layer by non-branched paraffins is anomalous. Pentadecane and hexadecane here exhibit contact angles of the same order of magnitude as those observed on the trimethylsiloxy surface. It was shown in the introduction that the surface concentration of the alkyl groups ($\Gamma = 4.1$ μmol)

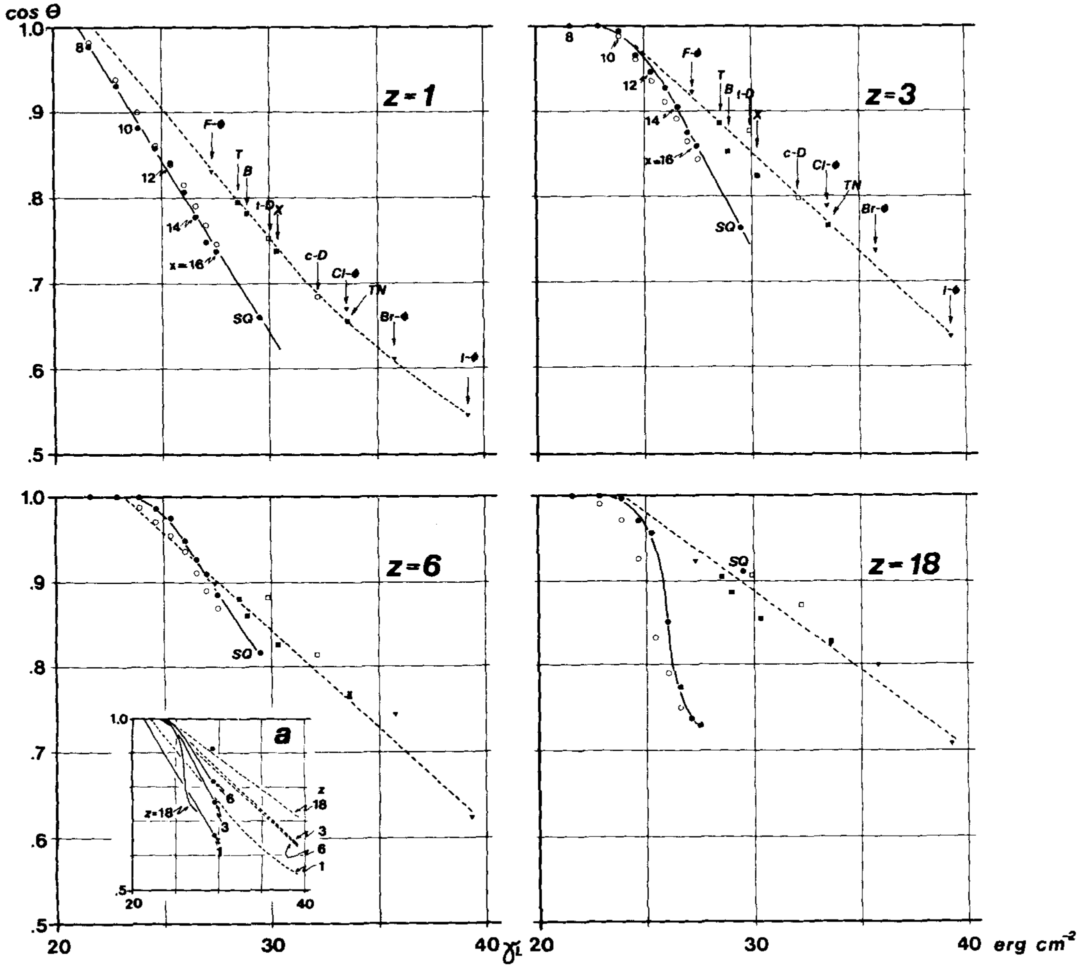

Fig. 2. *Cosine of wetting angles on methyl-* (z = 1), *propyl-* (z = 3), *hexyl-* (z = 6) *and octadecyl-* (z = 18)*-dimethylsiloxy layers on acid-leached glass, at 20°C, as a function of the surface tension of the wetting agent.*

Surface treatment: three consecutive periods at 250°C. For individual values see *Tables 4* and *5*. Wetting agents: x = 8 – 16: n-alkanes, C_xH_{2x+2}; SQ: squalane; *t*-D and *c*-D: *trans-* and *cis*-decalin; TN: 1,2,3,4-tetrahydronaphthalene; B, T and X: benzene, toluene and *o*-xylene; F-ϕ, Cl-ϕ, Br-ϕ and I-ϕ: fluoro-, chloro-, bromo- and iodobenzene. Open circles represent experimental results for n-paraffins on surfaces treated for three consecutive periods at 100°C/NH_3 catalyst (see *Table 7*).

is about half that of a crystalline arrangement. Consequently, it can be imagined that the surface layer can form a mixed crystal with a straight-chain wetting agent and that the wetting occurs on the exposed methyl groups at the surface of this layer. In 2.3, a detailed study of this phenomenon is presented.

2.3. *Wetting of alkyl-dimethylsiloxy layers by n-alkanes.* In 2.2 some of the results suggested that the alkyl groups anchored on the surface can form a sort of monomolecular mixed crystal with a n-alkyl wetting agent. It was questioned also, whether a molecular rough surface could enhance wettability. In fact, the ethyl-dimethylsiloxy surface can be considered as a roughened trimethylsiloxy layer because, in both cases, only methyl groups are exposed at the surface. In the work to be described it was intended to confirm these hypotheses by a systematic investigation. Capillaries were therefore prepared by treating them with methyl-, ethyl-, propyl-, hexyl-, decyl-, tetradecyl-, octadecyl- and docosyl-dimethylsilanol three times consecutively at 100 °C/ammonia catalyst. The wetting angles of n-alkanes were then determined at temperatures between 0° and 70 °C.

In *Figure 3,* the cosines of the wetting angles of n-alkanes are plotted as a function of the temperature and the length of the alkyl substituent at the surface. It is observed that the anomalous wetting behaviour of the tetradecyl-, octadecyl- and docosyl-dimethylsiloxy surfaces is confirmed at low temperatures and there seems to exist for each substance a transition temperature below which the surface is less wettable than above.

A simple steric consideration shows that the must regular surface crystals can be formed if $x=(z-2)$, where x is the carbon number of the wetting paraffin and z is the carbon number of the alkyl surface substituent. Such a crystal (*e.g.* hexadecane on octadecyl-dimethylsiloxy surface) should also have the lowest surface energy since it can form a smooth surface, covered with methyl groups and having all alkyl groups and alkanes in the extended conformation. In the case of longer or shorter inserted alkanes, the surface is either 'rough' on a molecular scale or the alkyl groups/alkanes must take up more energetic conformations in order to diminish the surface energy. The free energy difference, $\Delta F_{\mathrm{i}}^{*} = -\gamma_{\mathrm{LV}}\cos\theta$, is the specific free energy of immersion of a surface saturated with the vapour of the L^th^ wetting agent. Consequently, if there exists the possibility of formation of mixed surface crystals, $\Delta F_{\mathrm{i}}^{*}$ is the free energy of immersion of the surface *after* the mixed crystals has been formed. (The analogous enthalpy of wetting is then given by Eq. (34)). For a given surface, the family of the plots of $\Delta F_{\mathrm{i}}^{*}$ *versus* temperature for the n-alkanes were parallel and dit not deviate significantly from linearity. This means that the surface entropy, $\Delta s_{\mathrm{i}}^{*}$, was the same for all the substances.

The value of $\Delta F_{\mathrm{i}}^{*}$ can be considered as a measure of the surface free energy of the solid if the wetting agent is a paraffin. (By assuming *Zettlemoyer's* model, it is the dispersion part of the surface free energy of the solid, therefore its value should be independent of the wetting alkane (see 2.4)). In *Figure 4* the free energies, $\Delta F_{\mathrm{i}}^{*,0}$, are plotted as function of the carbon number of the wetting alkane. It is observed that they do not vary greatly between different alkanes on the same surface. For the octadecyl- and docosyl-substituted surfaces, $\Delta F_{\mathrm{i}}^{*,0}$-

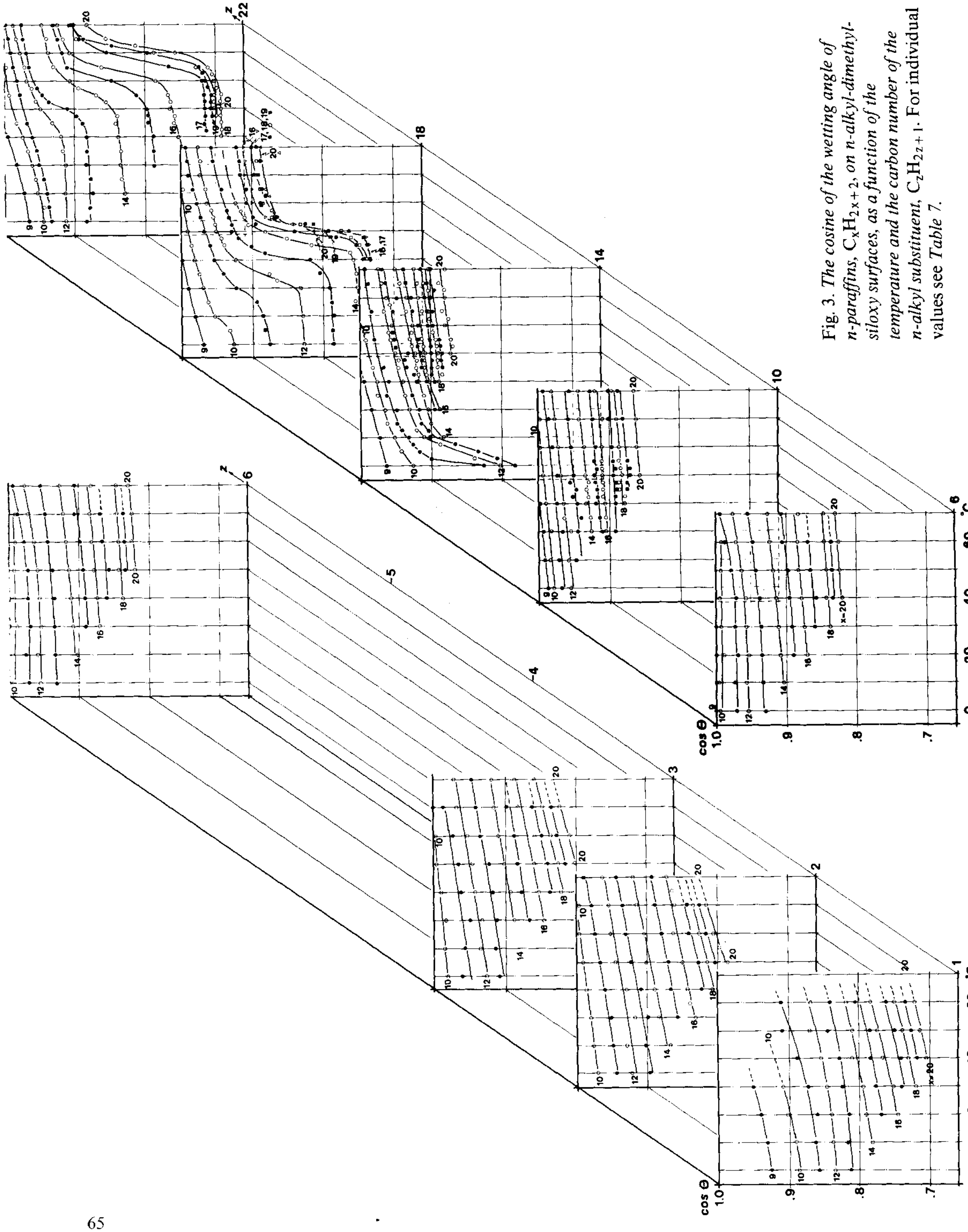

Fig. 3. *The cosine of the wetting angle of n-paraffins*, C_xH_{2x+2}, *on n-alkyl-dimethylsiloxy surfaces, as a function of the temperature and the carbon number of the n-alkyl substituent*, C_zH_{2z+1}. For individual values see *Table 7*.

values before and after the transition temperature were plotted. The values below the transition temperature are even lower than those for the trimethylsiloxy surface if the wetting agent is about two carbon atoms shorter than the anchored alkyl group. In *Figure 5*, the transition temperatures and the transition wetting entropies are plotted as a function of the difference between the carbon numbers of the wetting agent and of the surface alkyl. Negative values mean that the wetting alkane is the shorter of the two ($\Delta = x - z$). Both plots confirm that the least energetic mixed crystal is formed when $x \approx z - 2$. The transition temperature increases up to the alkane with carbon number $x = z - 2$, then it is more or less constant inspite of the increasing molecular weight.

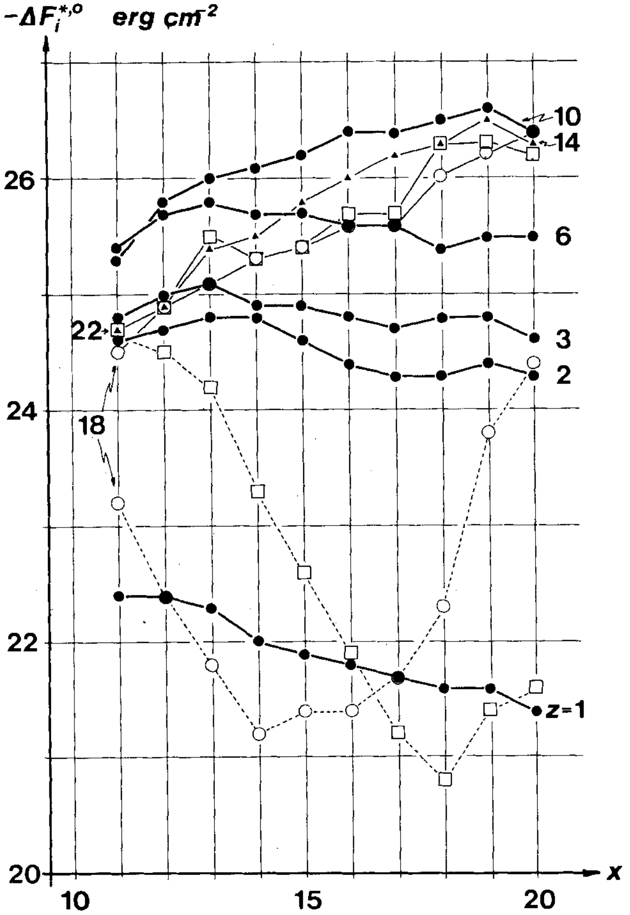

Fig. 4. *Free energy of immersion,* $\Delta F_i^{*,0}$ [erg cm^{-2}] at 0 °C, *on alkyl-dimethylsiloxy surfaces* (z is the carbon number of the alkyl substituent), *as a function of the carbon number of the wetting alkane, x*. For the surfaces with z = 18 and 22, open symbols, values connected with the full lines are observed above, those connected with dashed lines below, the transition temperature.

Let it be supposed that 'molecular roughness' is a reality, and that the ethyldimethyl surface can be considered as a rough, methylcovered surface. Under these assumptions, one can interpret the difference between the trimethyl and ethyl-dimethyl surfaces as being caused by roughness, and one can calculate following *Wenzel* [10], that

$$r=\frac{\cos\theta_{\mathrm{obs}}}{\cos\theta_{\mathrm{smooth}}}=\frac{\Delta F_{\mathrm{i}}^{*}\,(\mathrm{ethyl})}{\Delta F_{\mathrm{i}}^{*}\,(\mathrm{trimethyl})}=\frac{\Delta h_{\mathrm{i}}^{*}\,(\mathrm{ethyl})}{\Delta h_{\mathrm{i}}^{*}\,(\mathrm{trimethyl})}\,. \tag{4}$$

For n-alkanes as wetting agents the ratio of the free energies between 0° and 60° gives r = 1.11, and that of the enthalpies gives 1.15, - a reasonable agreement in view of the experimental error in the entropy term.

A detailed analysis of the wetting data presented in 2.4 reveals that this apparently obvious interpretation is probably wrong and that the better wettability of the ethyldimethyl surface can not be interpreted as being caused by 'molecular

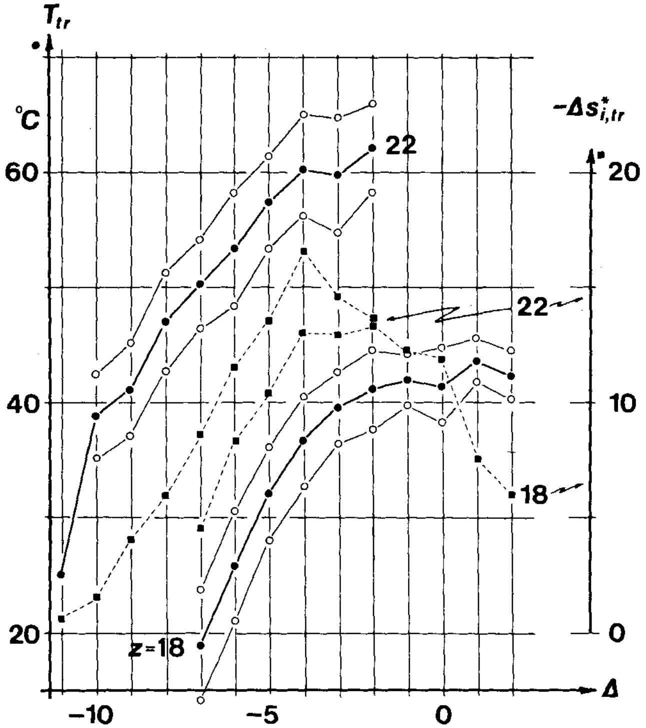

Fig. 5. *Transition temperature,* T_{tr}, *for surfaces deduced from wetting experiments as a function of the difference* $\Delta = x - z$ (where x is the carbon number of the wetting alkane and z is that of the surface alkyl substituent) *on octadecyl-* (z = 18) *and docosyl-dimethylsiloxy surfaces* (z = 22). The change of the free energy of immersion, $\Delta F_{\mathrm{i}}^{*}$, was appproximated by a Gaussian error function with the standard deviation σ_{tr}. Open symbols indicate $T_{tr}-\sigma_{tr}$ and $T_{tr}+\sigma_{tr}$. The change in the entropy of immersion $\Delta h^{*}_{\mathrm{i},tr}/T_{tr}(°\mathrm{K})=\Delta s^{*}_{\mathrm{i},tr}$ [erg cm^{-2} degree^{-1}], is also plotted (symbols connected with broken lines).

roughness'. Finally, it seems that surfaces covered by longer chains are swollen by the wetting agent. A possible model for the analysis of rough and of swollen surfaces will be proposed in 2.4.

2.4 *Wetting angles on rough and swollen surfaces.* Wetting angles are determined by the sum of three thermodynamic quantities

$$\gamma_{LV}\cos\theta = \gamma_S - \gamma_{SL} - \pi_{SV} \tag{5}$$

where γ_S is the free surface energy of the solid, γ_{SL} is the interfacial tension between the solid and the liquid, and π_{SV} is the surface pressure of the vapour of the wetting liquid on the solid. For solids having low surface energy *Fowkes* [11] proposes, following the ideas of *Girifalco & Good* [12], that

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma^d_{SV}\gamma^d_{LV}} \tag{6}$$

where γ^d_{SV} is the dispersion part of the free surface energy of the solid in equilibrium with the vapour of the wetting liquid and γ^d_{LV} is that part of the surface tension of the liquid which arises from the interaction, due to dispersion forces, between molecules. It is not believed that dispersion forces alone can act across an interface (*Fowkes* [6]). The data concerning the trimethylsiloxy surface *(Fig. 2)* clearly demonstrate that this dipolar surface is better wetted by polar/polarizable substances than by paraffins. Also *Zettlemoyer* [7] shows that heats of immersion can only be interpreted by assuming that dipolar forces can also act across an interface. However, the above hypothesis is certainly a very good approximation if either the solid or the wetting agent is a saturated hydrocarbon. Gas chromatographic data can be interpreted with success on the basis of the same hypothesis *i.e.* by considering paraffins, *and only paraffins,* as non-polarisable, non-polar matter [13-15].

Zettlemoyer [16] proposes an 'arithmetic mean model' giving, for the same quantity, γ_{SL}.

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - (\gamma^d_{SV} + \gamma^d_{LV})\,. \tag{7}$$

Finally, in both treatments it is supposed that the surface pressure, π_{SV}, is negligible for low energy solids, so that

$$\gamma^d_{SV} \approx \gamma^d_S. \tag{8}$$

With the aid of both models the surface energy of the solid, γ^d_S, can be calculated from wetting data on smooth surfaces.

Equations can also be derived for rough and swollen surfaces. The wetting angles on rough surfaces are given as a function of the wetting angle on smooth surfaces by *Wenzel's* Eq. (4). On a swollen surface a certain fraction, f, is composed of the original solid (in the swollen state), while the remainder, (1 - f), is covered by the wetting agent. Following the ideas of *Doss & Rao* [17] and *Cassie & Baxter* [18] for composite surfaces, wetting angle on the swollen surface is given by

$$\gamma_{LV}\cos\theta_{sw} = f(\gamma_{SV} - \gamma_{SL}) + (1-f)(\gamma_{WV} - \gamma_{WL}) \tag{9}$$

where the index W refers to the wetting agent dissolved at the surface of the swollen solid. In this over-simplified model, γ_{SV} is identified as the surface energy of the anchored alkyl chains, and γ_{SL} as the interfacial tension. Let it now be supposed that, on the fraction (1 - f) the surface energy, γ_{WV}, is equal to the surface tension of the wetting agent, γ_{LV}. In this case, the interfacial tension, γ_{WL}, equals 0 and equation (9) becomes

$$\gamma_{LV}\cos\theta_{sw} = f(\gamma_{SV} - \gamma_{SL}) + (1-f)\gamma_{LV}\,. \tag{10}$$

By assuming the approximation expressed in Eq. (8), and applying *Fowkes'* model, the combination of Eq. (6) with Eq. (4), (5) and (10), gives a set of relationships for the wetting angle on smooth (sm), rough (rh) and swollen (sw) surfaces. By introducing the variable ${}^{\mathrm{F}}\zeta = \sqrt{\gamma^{\mathrm{d}}_{\mathrm{LV}}}/\gamma_{\mathrm{LV}}$ for simplification, we get:

$$\cos\theta_{\mathrm{rh}} = -\mathrm{r} + 2\,\mathrm{r}\,{}^{\mathrm{F}}\zeta\sqrt{\gamma^{\mathrm{d}}_{\mathrm{S}}} \qquad \mathrm{r} > 1 \tag{11a}$$

$$\cos\theta_{\mathrm{sm}} = -1 + 2\,{}^{\mathrm{F}}\zeta\sqrt{\gamma^{\mathrm{d}}_{\mathrm{S}}} \tag{11b}$$

$$\cos\theta_{\mathrm{sw}} = (1 - 2\,\mathrm{f}) + 2\,\mathrm{f}\,{}^{\mathrm{F}}\zeta\sqrt{\gamma^{\mathrm{d}}_{\mathrm{S}}} \qquad 0 < \mathrm{f} < 1. \tag{11c}$$

Eq. 11a–c are linear functions of the variable ${}^{\mathrm{F}}\zeta$. They can be transformed to a single expression to give

$$\cos\theta = (1 - 2\,{}^{\mathrm{F}}\psi) + 2\,{}^{\mathrm{F}}\psi\,{}^{\mathrm{F}}\zeta\sqrt{{}^{\mathrm{F}}\gamma^{\mathrm{d}}_{\mathrm{S,obs}}} \tag{12}$$

where the index F refers to *Fowkes'* model and the parameters ${}^{\mathrm{F}}\psi$ and ${}^{\mathrm{F}}\gamma^{\mathrm{d}}_{\mathrm{S,obs}}$ are defined as follows:

Surface:	rough	smooth	swollen	
${}^{\mathrm{F}}\psi$	$=(1+\mathrm{r})/2$	1	f	(13)
${}^{\mathrm{F}}\gamma^{\mathrm{d}}_{\mathrm{S,obs}}$	$=[2\,\mathrm{r}/(1+\mathrm{r})]^2\gamma^{\mathrm{d}}_{\mathrm{S}}$	$\gamma^{\mathrm{d}}_{\mathrm{S}}$	$\gamma^{\mathrm{d}}_{\mathrm{S}}$.	(14)

In applying Eq. (12) to the evaluation of the experimental data first the parameters ${}^{\mathrm{F}}\psi$ and ${}^{\mathrm{F}}\gamma^{\mathrm{d}}_{\mathrm{S,obs}}$ have to be determined by a linear regression. The nature of the surface is then interpreted in function of the value of ${}^{\mathrm{F}}\psi$ in the following way

if	${}^{\mathrm{F}}\psi > 1$	${}^{\mathrm{F}}\psi = 1$	${}^{\mathrm{F}}\psi < 1$	
the surface is:	rough	smooth	swollen	
with	$\mathrm{r} = 2\,{}^{\mathrm{F}}\psi - 1$		$\mathrm{f} = {}^{\mathrm{F}}\psi$	(15)
and	$\gamma^{\mathrm{d}}_{\mathrm{S}} = \left(\frac{1+\mathrm{r}}{2\,\mathrm{r}}\right)^2 {}^{\mathrm{F}}\gamma^{\mathrm{d}}_{\mathrm{S,obs}}$	$\gamma^{\mathrm{d}}_{\mathrm{S}} = {}^{\mathrm{F}}\gamma^{\mathrm{d}}_{\mathrm{S,obs}}$	$\gamma^{\mathrm{d}}_{\mathrm{S,obs}}$.	(16)

It is important to note for the evaluation of the present data, that by using alkanes as wetting agents the following approximation can be applied

$$\gamma^{\mathrm{d}}_{\mathrm{LV}} = \gamma_{\mathrm{LV}} \equiv \gamma^{\mathrm{a}}_{\mathrm{LV}} \tag{17}$$

In this case the variable ${}^{\mathrm{F}}\zeta$ simplifies to ${}^{\mathrm{F}}\zeta^{\mathrm{a}} = 1/\sqrt{\gamma^{\mathrm{a}}_{\mathrm{LV}}}$.

Application of *Zettlemoyer*'s arithmetic mean model, Eq. (7), gives with Eq. (4), (5) and (10)

$$\cos\theta_{\mathrm{rh}} = -\mathrm{r} + \mathrm{r}(\gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{LV}}^{\mathrm{d}})/\gamma_{\mathrm{LV}} \qquad \mathrm{r} > 1 \tag{18a}$$

$$\cos\theta_{\mathrm{sm}} = -1 + (\gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{LV}}^{\mathrm{d}})/\gamma_{\mathrm{LV}} \tag{18b}$$

$$\cos\theta_{\mathrm{sw}} = (1-2\mathrm{f}) + \mathrm{f}(\gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{LV}}^{\mathrm{d}})/\gamma_{\mathrm{LV}} \qquad 0 < \mathrm{f} < 1\,. \tag{18c}$$

This set of Eq. can not be transformed into a single formula because the parameter, $\gamma_{\mathrm{S}}^{\mathrm{d}}$, and the variable, $\gamma_{\mathrm{LV}}^{\mathrm{d}}$, are not separable. Inspite of the apparent simplicity of these formulae, evaluation of experimental data is not straightforward as it is in the case of *Fowkes'* model.

However, by restricting the derivation to alkanes as wetting agents combination of (17) with (18) and introduction of the variable ${}^{\mathrm{Z}}\zeta^{\mathrm{a}} = 1/\gamma_{\mathrm{LV}}^{\mathrm{a}}$ gives an analogous expression to Eq. (12):

$$\cos\theta = (1 - {}^{\mathrm{Z}}\psi) + {}^{\mathrm{Z}}\psi\,{}^{\mathrm{Z}}\zeta^{\mathrm{a}}\,{}^{\mathrm{Z}}\gamma_{\mathrm{S,obs}}^{\mathrm{d}} \tag{19}$$

where the index Z refers to *Zettlemoyer*'s model, a, restricts attention to alkanes and the parameters ${}^{\mathrm{Z}}\psi$ and ${}^{\mathrm{Z}}\gamma_{\mathrm{S,obs}}^{\mathrm{d}}$ are defined as follows:

surface:	rough	smooth	swollen	
${}^{\mathrm{Z}}\psi$ =	1	1	f	(20)
${}^{\mathrm{Z}}\gamma_{\mathrm{S,obs}}^{\mathrm{d}}$ =	$\mathrm{r}\gamma_{\mathrm{S}}^{\mathrm{d}}$	$\gamma_{\mathrm{S}}^{\mathrm{d}}$	$\gamma_{\mathrm{S}}^{\mathrm{d}}$	(21)

The interpretation of the regression parameters on the experimental data is now

if	${}^{\mathrm{Z}}\psi > 1$	${}^{\mathrm{Z}}\psi = 1$	${}^{\mathrm{Z}}\psi < 1$	
the surface is:	(no physical meaning)	rough or smooth	swollen	
with		$\mathrm{r} \geqslant 1$	$\mathrm{f} = {}^{\mathrm{Z}}\psi$	(22)
and		$\gamma_{\mathrm{S}}^{\mathrm{d}} = {}^{\mathrm{Z}}\gamma_{\mathrm{S,obs}}^{\mathrm{d}}/\mathrm{r}$	$\gamma_{\mathrm{S}}^{\mathrm{d}} = {}^{\mathrm{Z}}\gamma_{\mathrm{S,obs}}^{\mathrm{d}}$.	(23)

Thus the value of the parameter, r, can not be determined and on rough surfaces $\gamma_{\mathrm{S}}^{\mathrm{d}}$ can not be calculated. However, this result gives a method to apply the set of Eq. (18) to experimental data. First wetting angles are determined with agents including alkanes. The data of the alkanes are evaluated with Eq. (19) giving two cases:

If ${}^{\mathrm{Z}}\psi < 1$ Eq. (18c) should be applied to all data, if ${}^{\mathrm{Z}}\psi \geqslant 1$ Eq. (18a) is to be used.

Before applying the derived formulae to the evaluation of the experimental data, it is interesting to complete this analysis by comparing them with *Zisman's* empirical formula

$$\cos\theta = 1 + b(\gamma_{LV}^{a} - \gamma_c) \tag{24}$$

which implies that a plot of the cosines of the wetting angles versus γ_{LV}^{a} is linear, the intersection with the horizontal at $\cos\theta = 1$ giving γ_c, the 'critical surface tension' of the solid [8]. (One continues here to restrict attention to paraffins as wetting agents).

If Eq. (12) and (19) are represented on a '*Zisman* plot' ($\cos\theta$ *versus* γ_{LV}^{a}) curves are obtained having intersections with the horizontal, $\cos\theta = 1$, at a certain γ_{LV}^{a}, corresponding to $\gamma_{S,obs}^{d}$, as illustrated in *Figure 6* ($u = \gamma_{LV}/\gamma_{S,obs}^{d}$). One can calculate the value of the slope, a, at $\cos\theta = 1$ as

$$a = -\psi/\gamma_{S,obs}^{d} \tag{25}$$

where the parameter ψ can be either ${}^{F}\psi$ or ${}^{Z}\psi$ as defined by Eq. (13) and (20). Eq. (25) permits a rough estimation of the parameter ψ. Let it now be supposed that experimental points have been determined in the range: $\cos\theta = y_0$ to $\cos\theta = 1$, and γ_c and b of Eq. (24) has been determined by a linear regression.

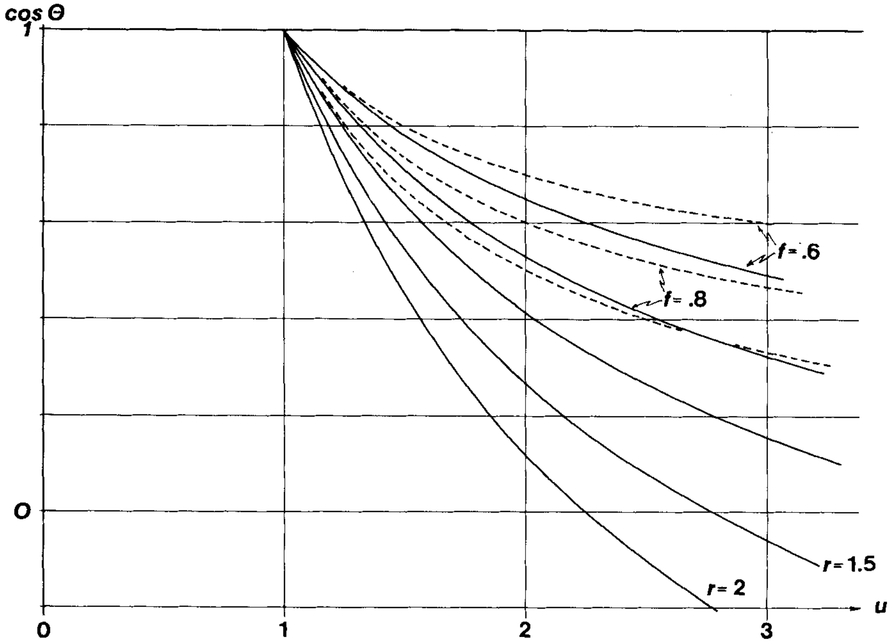

Fig. 6. *A plot of the equations describing the variation of the cosine of the contact angle as a function of the dimensionless variable,* $u = \gamma_{LV}^{a}/\gamma_{S,obs}^{d}$, *for rough, smooth and swollen surfaces.* Solid lines: *Fowkes'* model; dashed lines: *Zettlemoyer's* model for the interfacial tension γ_{SL}^{d}.

In the experimental section (chapter 3) the derivation of the relationship between $\gamma^{d}_{S,obs}$ and γ_c is given as a function of the slope b of the linear regression and the limit, y_0, of the experimental domain. In order to find $\gamma^{d}_{S,obs}$, the procedure is as follows. First the value of the variable w (or, which is equivalent, $\psi = (1-y_0)/w$) is calculated. By solving Eq. (41) and (42) (see chapter 3) we obtain the approximations

Fowkes $$w \approx \sqrt{(40\,p+30)^2+80} - (40\,p+30) \tag{26}$$

Zettlemoyer $$w \approx \sqrt{(7.5\,p+7.5)^2+15} - (7.5\,p+7.5) \tag{27}$$

where $p = \gamma_c b/(1-y_0)$.

In the experimental domain $0.6 < y_0 < 1$ and $0.5 < \psi < 2$, the error introduced on ψ by this approximation is less than 2‰ when using *Fowkes'* model and 2% with *Zettlemoyer's* model. Having found w from the experimental data, we can now calculate the factor ϕ defined by

$$\gamma^{d}_{S,obs} = \phi\,\gamma_c \tag{28}$$

by means of Eq. (43) and (44). These relationships permit the interconversion and comparison of results obtained by different methods.

In order to illustrate the use of the equations obtained and the limits of the method, the critical surface tension, γ_c, the observed dispersion part of the specific surface energy, $\gamma^{d}_{S,obs}$, the roughness, r, the swelling resistance, f, and the dispersion part of the specific surface energy of the solid, γ^{d}_{S}, are given for different alkyl-dimethylsiloxy surfaces in *Table 3*. The values were calculated by applying the derived formulae and by using experimental wetting angles determined with the wetting agents undecane to eicosane. In the case of octadecyl- and docosyl-dimethylsiloxy surfaces, only wetting angles for the 'molten' surfaces have been considered.

It is now interesting to compare the figures calculated by different methods. First *(Fig. 7)*, the observed specific surface free energies ($\gamma^{d}_{S,obs}$) are very nearly the same whether calculated with the geometric or arithmetic mean model (${}^{F}\gamma^{d}_{S}$ and ${}^{Z}\gamma^{d}_{S}$) but their values are always higher than the critical surface tension, γ_c. A slight error is introduced if they are calculated *via* γ_c with the corrections deduced above. The same regularities are observed for the surface entropy ($= -\partial\gamma^{d}_{S,obs}/\partial T$). The parameter ψ is nearly independent of the temperature (as it should be) but its value shows important differences in the two models in that the arithmetic mean model (${}^{Z}\psi$) results in values some 8% higher *(Fig. 8)*. The estimation *via* the slope of *Zisman's* plot always gives low values for ψ. Values of ${}^{Z}\psi > 1$ have no physical meaning in the arithmetic mean model. In the geometric-mean model they are related to the roughness factor ($r = 2\,\psi - 1$). Therefore, the results for the surface free energy, γ^{d}_{S}, are quite different if the surface appears rough in *Fowkes'* model. This is also the case for the dispersion part of the surface energies, h^{d}_{S}.

As for the physical meaning, it is difficult to understand the results obtained on surfaces with short alkyl chains. The interpretation of the wettability of the ethyl-dimethylsiloxy surface as a molecularly rough trimethyl surface (given in 2.3) seems to be quite satisfactory, but clearly contradicts the values of r obtained from *Fowkes'* model. These would suggest that the rough surface of the acid leached glass is gradually smoothed by ethyl and propyl substituents, being an

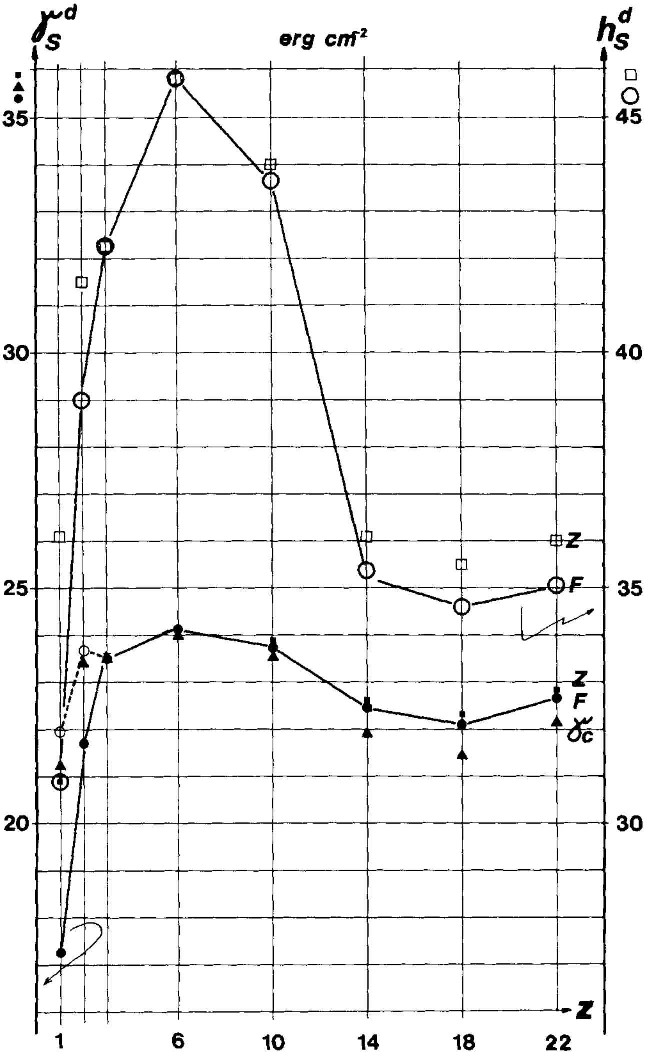

Fig. 7. *The critical surface tension,* γ_c, *the dispersion part of the specific free surface energy,* γ_S^d, *and of the surface enthalpy,* h_S^d, *as a function of the carbon number,* z, *of surfaces covered by* n-C_zH_{2z+1}-*dimethylsiloxy groups.* Full symbols refer to, γ_S^d, open symbols to, h_S^d, with the exception of small open circles marking the observed specific surface energy, $\gamma_{S,obs}^d$, calculated from *Fowkes'* model. Values calculated with *Fowkes'* model are marked by F, those calculated with *Zettlemoyer's* model by Z.

ideal plane if covered by propyl-dimethylsiloxy groups. This interpretation would be supported by the experimental observation that in repeated preparations the wetting angles on trimethylsiloxy surfaces were poorly reproducible contrary to ethyl and higher substituted surfaces. Following *Bikermann* [19] the roughness factor of cleaned glass beads is 1.6 thereby supporting that it could be 1.26 for the trimethylsiloxy surface. Finally a value of 17.4 erg cm^{-2} for its surface free energy (at 20 °C) is in good agreement with the value found on dimethylsilicones of 16.9 ± 0.5 [20].

Table 3. *Critical surface tension,* γ_c, *observed dispersion part of the specific surface energy,* $\gamma^{d}_{S,obs}$, *roughness,* r, *swelling resistance* (expressed as the fraction of the non-swollen surface of the solid), f, *the dispersion part of the specific surface free energy of the solid,* γ^{d}_{S}, *all values at 20°C and the specific surface enthalpy,*

R			Methyl		Ethyl		Propyl	
X		Regression with the ind. variable	X	10 (∂X/∂T)	X	10 (∂X/∂T)	X	10 (∂X/∂T)
γ_c	erg cm^{-2}	γ^{a}_{LV}	21.2	−0.51	23.3	−0.60	23.5	−0.61
b	$erg^{-1} cm^{2}$	γ^{a}_{LV}	−0.038	−0.002	−0.037	−0.002	−0.035	−0.002
${}^{F}\gamma^{d}_{S,obs}$	erg cm^{-2}	$1/\sqrt{\gamma^{a}_{LV}}$	21.9	−0.58	23.6	−0.64	23.7	−0.65
		γ^{a}_{LV} + corr	21.5	−0.53	23.5	−0.61	23.6	−0.62
${}^{Z}\gamma^{d}_{S,obs}$	erg cm^{-2}	$1/\gamma^{a}_{LV}$	22.1	−0.60	23.6	−0.65	23.8	−0.66
		γ^{a}_{LV} + corr	21.5	−0.53	23.5	−0.61	23.6	−0.64
${}^{F}\psi$	-	$1/\sqrt{\gamma^{a}_{LV}}$	1.138[a])	(0.000)	1.046[a])	(0.001)	1.005[a])	(0.002)
		γ^{a}_{LV} + corr	1.047[a])	(0.010)	1.021[a])	(0.010)	0.971	0.010
${}^{Z}\psi$	-	$1/\gamma^{a}_{LV}$	1.245	−0.004	1.107	−0.002	1.060	−0.001
		γ^{a}_{LV} + corr	1.114	0.009	1.058	0.010	1.021	0.010
${}^{F}r$	-	$1/\sqrt{\gamma^{a}_{LV}}$	1.276[a])	(0.000)	1.092[a])	(0.002)	1.010[a])	(0.004)
		γ^{a}_{LV} + corr	1.094[a])	(0.020)	1.042[a])	(0.020)		–
${}^{F}f$	-	$1/\sqrt{\gamma^{a}_{LV}}$	–		–			–
		γ^{a}_{LV} + corr	–		–		0.971	0.010
${}^{Z}f$	-	$1/\gamma^{a}_{LV}$	–		–			–
		γ^{a}_{LV} + corr	–		–			–
${}^{F}\gamma^{d}_{S}$	erg cm^{-2}	$1/\sqrt{\gamma^{a}_{LV}}$	17.4	−0.46	21.7	−0.59	23.5	−0.64
		γ^{a}_{LV} + corr	19.7	−0.53	22.6	−0.59	23.6	−0.62
${}^{Z}\gamma^{d}_{S}$	erg cm^{-2}	$1/\gamma^{a}_{LV}$	20.9[b])	−0.52	23.3[b])	−0.62	23.6[b])	−0.64
		γ^{a}_{LV} + corr	21.7[b])	−0.53	23.5[b])	−0.61	23.6[b])	−0.62
${}^{F}h^{d}_{S}$	erg cm^{-2}	$1/\sqrt{\gamma^{a}_{LV}}$	30.9		39.0		42.3	
		γ^{a}_{LV} + corr	35.2		39.9		42.4	
${}^{Z}h^{d}_{S}$	erg cm^{-2}	$1/\gamma^{a}_{LV}$	36.1[b])		41.5[b])		42.4[b])	
		γ^{a}_{LV} + corr	37.2[b])		41.4[b])		41.8[b])	

[a]) Mean values, supposing that the roughness does not change with temperature (values at 30° for the surface R = methyl and at 35° for ethyl and propyl). [b]) In this model a value of $\psi > 1$ has no interpretation.

Surfaces covered with tetradecyl and longer chains represent typical swollen surfaces. In the introduction it has been shown that the surface density of the alkyl chains is about one half of that in compressed monolayers or in a polyethylene crystal, hence, the value of the fraction covered with the fixed alkyl chains, f, should be about 0.50. The value deduced from wetting experiments is about 0.55. The agreement is very satisfactory. It is observed that for such surfaces the surface entropy, s^d_S, is smaller (the half) compared to those covered with shorter chains.

h^d_S, *of R-dimethylsiloxy surfaces, calculated as described in the text. (For the definition of* $\mathfrak{b}$, *see Eq. (24)).* Temperature dependences for 10 °C are also given.

Hexyl		Decyl		Tetradecyl		Octadecyl		Docosyl	
X	10 (∂X/∂T)	X	10 (∂X/∂T)	X	10 (∂X/∂T)	X	10 (∂X/∂T)	X	10 (∂X/∂T)
24.0	−0.72	23.5	−0.65	21.9	−0.35	21.5	−0.33	22.1	−0.34
−0.035	−0.001	−0.025	−0.001	−0.018	−0.001	−0.019	−0.001	−0.020	−0.001
24.1	−0.74	23.8	−0.68	22.4	−0.44	22.1	−0.43	22.6	−0.43
24.1	−0.72	23.7	−0.66	22.1	−0.37	21.7	−0.35	22.4	−0.36
24.2	−0.74	23.8	−0.69	22.6	−0.46	22.3	−0.45	22.8	−0.45
24.1	−0.72	23.7	−0.66	22.2	−0.38	21.8	−0.36	22.4	−0.37
0.975	0.000	0.694	0.005	0.533	0.009	0.545	0.010	0.582	0.010
0.957	0.005	0.680	0.010	0.500	0.018	0.494	0.017	0.544	0.019
1.023	−0.001	0.733	0.003	0.577	0.006	0.595	0.006	0.628	0.005
1.001	0.006	0.716	0.010	0.536	0.017	0.528	0.016	0.579	0.017
	–		–		–		–		–
	–		–		–		–		–
0.975	0.000	0.694	0.005	0.533	0.009	0.545	0.010	0.582	0.010
0.957	0.005	0.680	0.010	0.500	0.018	0.494	0.017	0.544	0.019
	–	0.733	0.003	0.577	0.006	0.595	0.006	0.628	0.005
	–	0.716	0.010	0.536	0.017	0.528	0.016	0.579	0.017
24.1	−0.74	23.8	−0.68	22.4	−0.44	22.1	−0.43	22.6	−0.43
24.1	−0.72	23.7	−0.66	22.1	−0.37	21.7	−0.35	22.4	−0.36
24.1b)	−0.74	23.8	−0.69	22.6	−0.46	22.3	−0.45	22.8	−0.45
24.1b)	−0.72	23.7	−0.66	22.2	−0.38	21.8	−0.36	22.4	−0.37
45.8		43.7		35.3		34.7		35.2	
45.2		43.0		33.0		32.0		33.0	
45.8b)		44.0		36.1		35.5		36.0	
45.2b)		43.0		33.3		32.4		33.2	

Therefore, a new regression has been made by supposing the value of $\psi = 1$, so that the reported value is $r^Z\gamma^d_S$ (if the surface is rough), but r cannot be deduced with Zettlemoyer's model.

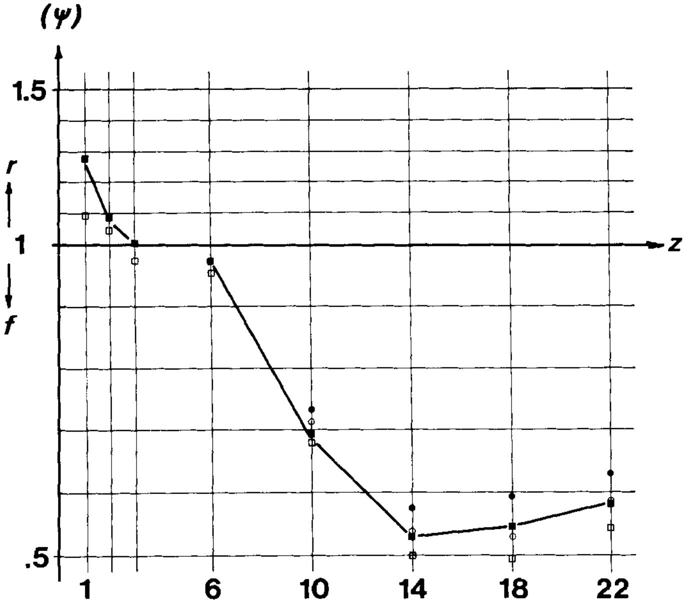

Fig. 8. *The value of the parameter, ψ, as a function of the carbon number, z, on surface covered by n-C_zH_{2z+1}-dimethylsiloxy substituents.* The line connects the values calculated with *Fowkes'* model, full circles are calculated with *Zettlemoyer's* model. Open symbols are values estimated from the slope of the '*Zisman* plot' as described in the text.

Finally, the properties of hexyl- and decyl-dimethylsiloxy surfaces are intermediate between the two extremes. They are swollen *and* the surface energy is the highest and can be considered as optimum in this series if maximum wettability is demanded.

2.5. *Final remarks.* The formation of mixed surface crystals has been well established. The calorimetric determination of their melting enthalpy shall be the subject of a forthcoming paper. The existence of mixed surface films, which could be crystalline, has been described repeatedly in literature. If monofunctional non-branched alkyl derivatives are adsorbed on a metal surface from their solution in n-alkanes, a certain amount of solvent is incorporated in the film [21-23]. The situation in these films is somewhat analogous to that described in the present paper. In such films only the alkyl derivative is anchored on the metal and the alkane is retained by lateral interactions. Of course in such a case the ratio of the concentrations of the two components of the film can be different. *Bewig & Zisman* have shown [24] that the highest amounts of alkanes are incorporated in alkylamine layers if the chain length of the alkylamine and that of the alkane is equal. Under well defined conditions the amount of alkane incorporated was constant (~15 mol%) for C_{14}, C_{16} and C_{18} amines, suggesting a crystalline arrangement. Mixed layers of even closer analogy are described by *Kuhn et al.* Films with octadecyl-substituted dyes can be stiffened by incorporating arachidic acid or octadecane [25]. The dimension of the polar head is such that in a compressed monolayer the layer of the alkyl groups is sparse, the layer can only be crystallised if a definite molar ratio of octadecane is incorporated [26].

Surfaces with longer substituents are good models for the study of the wetting properties of materials or films which can be swollen. The equations relating the wettability of such surfaces with the degree of swelling show that care must be taken in deducing surface free energies from an insufficient number of measurements. Actually, the incorporation of a second parameter in *Fowkes'* or *Zettlemoyer*'s equation (ψ) demonstrates that the equation is only a 'one-parameter-equation' if the surface is an ideal plane, and that the second parameter can be interpreted in terms of roughness or swollenness. In cases where this parameter indicated a swollen surface the value of the degree of swelling was in good agreement with the value estimated from other sources.

This work is a report on a part of a project supported by the *'Fonds National Suisse de la Recherche Scientifique'.* One of us *(M.C.)* thanks the *'Scientific Exchange Agreement'* for financial help.

Experimental Part

Alkyl-dimethylsilanols. The synthesis and purity of the coating materials is described in [27].

The *wetting liquids* were research grade products supplied by *Fluka AG* (Buchs, Switzerland). All the commercially available substances were first purified by fractional distillation from which the fore-run and residue (each equal to 10%) were discarded. The middle fraction was then filtered through a silica gel column (comprising 20% by weight of the substance to be purified) and stored in a glass-stoppered flask. Octadecane, nonadecane and eicosane were also recrystallized from ether/methanol. The purity, determined by gas chromatography, was always better than 99.5%. The densities and surfaces tensions are summarized in *Table 4.*

The *glass capillaries* were drawn from precision Pyrex tube using a *Hupe & Busch* (Karlsruhe, Germany) glass drawing apparatus. The capillaries (inner diameter, 0.200±0.001 mm) were then cut into lengths of 10 cm and immerged in nitric acid (puriss; 65%). After two days, they were washed in distilled water, and dried in a stream of nitrogen at 60°C for 6 h in preparation for use for the surface treatment.

Surface treatment. Method a): The inner surface of the dry, acid leached capillary was wetted with an R-dimethylsilanol, by letting a droplet of the pure substance flow through it. Some twenty capillaries were then placed in a small diameter ampule. If the silanol applied had the substituent R = decyl or shorter, the ampule was cooled with liquid nitrogen, evacuated to 0.1 Torr, and sealed. For silanols of higher molecular weight, this operation was carried out at room temperature. The ampules were then placed, overnight, in a thermostated oven at 250°C. The capillaries were then washed with distilled diethyl ether and dried in a stream of nitrogen for 6 h at 60°C. This treatment was repeated two more times for the already treated capillaries.

Method b): The capillaries were wetted and placed in an ampule which was evacuated, as described above by using a three way stop-cock open to the vacuum pump side. The ampule was then cooled with liquid nitrogen (except for silanols of higher molecular weight, see method a)) and evacuated to 0.1 Torr. After closing the three way stop-cock, it was allowed to warm up to room temperature, and connected to a bottle filled with ammonia vapor at about 200 Torr. Finally, the ampule was sealed, and placed overnight in a thermostated oven at 100°. Washing, drying and the repeated treatments (three in all) were as described above.

Measurement of the capillary rise. The capillaries (maximum 20) were placed in a support fixed to an airtight cap. The cap fitted a cylindrical vessel, made from a precision tube of 5 cm i.d. in order to avoid parallax effects. The wetting agent (10 ml) was placed in this vessel, the

Table 4. *Physical properties of the wetting agents:* density at 20°C, ρ_L^{20}; coefficient of thermal expansion, *k*; surface tension at 20°C; γ_L^{20}; and temperature coefficient of the surface tension $\partial\gamma_L/\partial T$. For surface tensions see also [38].

	ρ_L^{20} g cm^{-3}	$10^3 k$ degree^{-1}	Temp. domain. °C	Ref.	γ_L^{20} erg cm^{-2}	10^3 $(\partial\gamma_L/\partial T)$ erg cm^{-2} degree^{-1}	Temp. domain. °C	Ref.
Paraffins								
Hexane	0.659	1.41	0-60	[28]	18.40	−102.2	0- 60	[29]
Heptane	0.684	1.31	0-80	[28]	20.14	−98.0	0- 90	[29]
Octane	0.703	1.20	0-80	[28]	21.62	−95.09	0-120	[29]
Nonane	0.718	1.15	0-80	[28]	22.85	−93.47	0-120	[29]
Decane	0.730	1.07	0-80	[28]	23.83	−91.97	0-120	[29]
Hendecane	0.740	1.02	0-80	[28]	24.66	−90.10	0-120	[29]
Dodecane	0.749	0.98	0-80	[28]	25.35	−88.43	0-120	[29]
Tridecane	0.756	0.94	0-80	[28]	25.99	−87.19	0-120	[29]
Tetradecane	0.763	0.91	10-80	[28]	26.56	−86.88	30-120	[29]
Pentadecane	0.768	0.92	10-80	[28]	27.07	−85.65	30-120	[29]
Hexadecane	0.774	0.90	20-80	[28]	27.47	−85.40	30-120	[29]
Heptadecane	(0.778[a])	0.90	20-80	[28]	(27.91[a])	−84.60	30-120	[29]
Octadecane	(0.783[a])	0.90	20-80	[28]	(28.29[a])	−84.28	30-120	[29]
Nonadecane	(0.786[b])	0.86	30-80	[28]	(28.59[b])	−83.73	30-120	[29]
Eicosane	(0.787[b])	0.81	30-80	[28]	(28.87[b])	−83.29	30-120	[29]
Squalane	0.810				29.5	−90	20- 50	
Cyclic hydrocarbons								
cis-Decalin	0.897	0.85	20-30	[30]	32.05	−109.2	0- 80	[31]
trans-Decalin	0.870	0.86	20-30	[30]	29.87	−100.4	0- 80	[31]
Benzene	0.879	1.21	20-30	[26]	28.87	−129.1	10- 80	[28]
Toluene	0.867	1.06	20-25	[28]	28.52	−118.9	10-100	[32]
o-Xylene	0.880	0.96	20-25	[28]	30.31	−110.1	10-100	[33]
Tetralin	0.970	0.83	20-25	[28]	33.64	− 95.4	20-85	[34]
Halogenobenzenes								
Fluorobenzene	1.023				27.26	−120.4	10- 80	[35]
Chlorobenzene	1.106	0.94	20-25	[36]	33.59	−119.1	10-130	[35]
Bromobenzene	1.495	0.91	20-25	[37]	35.82	−116.0	10-150	[35]
Iodobenzene	1.831				39.27	−112.3	10-160	[35]

[a] Undercooled liquid. [b] Extrapolated value.

support inserted, and a slow stream of nitrogen passed through a hole in the cap. Five such vessels were placed in a thermostated water bath provided with a plane-parallel window. The height of the liquid in the capillary was measured using a *Spindler & Hoyer* (Göttingen, Germany) cathetometer.

Determination of contact angles. - Principle: The height of the rise in a capillary is given by

$$h_{L,j} = \frac{g r_j \rho_L}{2\gamma_{LV}\cos\theta_{L,j}} = K_j \frac{\rho_L}{\gamma_{LV}\cos\theta_{L,j}} \tag{29}$$

where $h_{L,j}$ is the height of capillary rise of the Lth substance in the jth capillary, g is the acceleration due to gravity, r_j is the radius of the capillary, ρ is the specific mass of the liquid, γ_{LV} is the surface tension, θ is the contact angle and K_j is the constant of the jth capillary ($= g r_j/2$). By

Table 5. *Cosine of contact angles at 20°C on surfaces covered by R-dimethylsiloxy groups after A: one treatment and B: three successive treatments using the corresponding silanols at 250°/8 h without a catalyst* (method a). R is a non-branched substituent C_zH_{2z+1}. Average of three measurements. The difference $\delta = \cos\theta_B - \cos\theta_A$.

	Methyl (z = 1)			Propyl (z = 3)			Hexyl (z = 6)			Octadecyl (z = 18)		
	A	B	δ	A	B	δ	A	B	δ	A	B	δ
Paraffins												
Octane	0.983	0.975	−0.008	0.997	1.000	+0.003	1.000	0.998	−0.002	0.998	0.998	0.000
Nonane	0.948	0.931	−0.017	0.999	1.002	+0.003	1.000	1.002	+0.002	1.000	1.002	+0.002
Decane	0.905	0.881	−0.024	0.994	0.992	−0.002	0.994	1.000	+0.006	0.990	0.998	+0.008
Hendecane	0.877	0.857	−0.020	0.982	0.965	−0.017	0.995	0.988	−0.007	0.980	0.982	+0.002
Dodecane	0.840	0.834	−0.006	0.958	0.943	−0.015	0.974	0.974	0.000	0.952	0.960	+0.008
Tridecane	0.815	0.806	−0.009	0.935	0.927	−0.008	0.943	0.950	+0.007	0.849	0.850	+0.001
Tetradecane	0.789	0.778	−0.011	0.905	0.916	+0.011	0.925	0.930	+0.005	0.769	0.773	+0.004
Pentadecane	0.768	0.747	−0.021	0.886	0.876	−0.010	0.904	0.908	+0.004	0.736	0.741	+0.005
Hexadecane	0.749	0.737	−0.012	0.862	0.850	−0.012	0.888	0.885	−0.003	0.733	0.727	−0.005
Squalane	0.671	0.659	−0.012	0.789	0.776	−0.013	0.819	0.817	−0.002	0.908	0.910	+0.002
Cyclic hydrocarbons												
cis-Decalin	0.681	0.683	+0.002	0.802	0.797	−0.005	0.828	0.814	−0.014	0.868	0.866	−0.002
trans-Decalin	0.753	0.750	−0.003	0.877	0.870	−0.007	0.882	0.880	−0.002	0.905	0.905	0.000
Aromatic hydrocarbons												
Benzene	0.808	0.781	−0.027	0.881	0.851	−0.030	0.874	0.859	−0.015	0.893	0.885	−0.008
Toluene	0.822	0.794	−0.028	0.904	0.886	−0.018	0.886	0.883	−0.003	0.906	0.908	+0.002
o-Xylene	0.765	0.736	−0.029	0.845	0.823	−0.022	0.845	0.828	−0.017	0.864	0.854	−0.010
Tetralin	0.677	0.655	−0.022	0.768	0.767	−0.001	0.777	0.768	−0.009	0.834	0.834	0.000
Halogenobenzenes												
Fluorobenzene	0.886	0.830	−0.056	0.943	0.922	−0.021	0.918	0.898	−0.020	0.930	0.923	−0.007
Chlorobenzene	0.714	0.671	−0.043	0.783	0.786	+0.003	0.783	0.766	−0.017	0.825	0.822	−0.003
Bromobenzene	0.658	0.610	−0.048	0.735	0.734	−0.001	0.734	0.751	+0.017	0.797	0.799	+0.002
Iodobenzene	0.579	0.546	−0.033	0.632	0.635	+0.003	0.651	0.625	−0.026	0.706	0.719	+0.013

using a liquid, L*, which wets the surface completely ($\cos\theta = 1$), the capillary constant can easily be determined from

$$K_j = \frac{\gamma_{L^*} v}{h_{L^*,j} \rho_{L^*}} . \tag{30}$$

Calibration. For each capillary the constant, K_j, was determined using hexane and heptane at 20 °C. For a series of capillaries drawn from the same tube the constant, K, was the same.

Measurement. The L^th^ wetting agent was placed in the vessel, the height measured at the given temperature and the cosine of the angle calculated from

$$\cos\theta = K \frac{\rho_L}{h_L \gamma_{LV}} . \tag{31}$$

Contact angles on surfaces treated by method a). Batches of some 30 capillaries were treated with methyl-, propyl-, hexyl- and octadecyl-dimethylsilanol using method a) (one treatment): capillary A; the half of them were then treated again two more times: capillary B. On every support were fixed groups of three capillaries, A and B, including every type of coating agent and the rise of wetting liquids determined at 20 °C. The cosine of the wetting angles are given by *Table 5.*

In a second series of experiments receding and advancing contact angles were determined on a new batch of capillaries treated three times using method a). In this series were also included capillaries treated by ethyl-, decyl-, tetradecyl- and docosyl-dimethylsilanol. The results are summarized in *Table 6.*

Contact angles on surfaces treated by method b). Some 20 capillaries were treated three successive times with methyl-, ethyl-, propyl-, hexyl-, decyl-, tetradecyl-, octadecyl- or docosyl-dimethylsilanol, using method b: capillary C. The height of capillary rise of n-hydrocarbons was determined, by two different operators, at temperatures between 0 and 70 °C. The results are summarized in *Table 7.*

Regression equation for the free energy of immersion, ΔF_i^*, as a function of temperature (the 'adhesion tension' of Freundlich [39]*).* (Note that the free energy of immersion ΔF_i is defined as

Table 6. *Cosine of advancing* (a) *and receeding* (r) *contact angles at 20°C of n-paraffins on chemisorbed monolayers of alkyl-dimethylsiloxy substituents.* Surface treatment by method a), three successive treatments: capillary B. Capillary rise method. Average of three measurements.

		Methyl	Ethyl	Propyl	Hexyl	Decyl	Tetradecyl	Octadecyl	Docosyl
Nonane	a	0.950	1.005	1.006	1.005	1.004	0.996	1.001	0.998
	r	0.949	1.004	1.006	1.005	1.003	0.996	1.001	0.997
Decane	a	0.907	0.984	0.991	0.995	0.988	0.974	0.980	0.973
	r	0.904	0.986	0.991	0.995	0.987	0.973	0.981	0.977
Hexadecane	a	0.872	0.958	0.963	0.974	0.972	0.953	0.955	0.952
	r	0.872	0.960	0.962	0.981	0.972	0.953	0.955	0.959
Dodecane	a	0.845	0.930	0.944	0.960	0.961	0.938	0.923	0.919
	r	0.843	0.928	0.941	0.964	0.960	0.937	0.921	0.918
Tridecane	a	0.824	0.906	0.915	0.933	0.943	0.921	0.820	0.870
	r	0.825	0.911	0.918	0.932	0.944	0.920	0.838	0.876
Tetradecane	a	0.795	0.889	0.893	0.912	0.934	0.918	0.751	0.826
	r	0.797	0.894	0.900	0.908	0.936	0.918	0.751	0.824
Pentadecane	a	0.777	0.868	0.878	0.892	0.918	0.910	0.726	0.786
	r	0.779	0.870	0.879	0.892	0.923	0.911	0.731	0.785
Hexadecane	a	0.751	0.843	0.852	0.872	0.902	0.899	0.709	0.739
	r	0.762	0.851	0.856	0.874	0.904	0.900	0.715	0.758

Table 7. *Cosine of the wetting angle of n-alkanes,* C_xH_{2x+2}, *on glass surfaces covered by n-alkyl-dimethylsiloxy substituents.* Acid leached Pyrex capillaries of approximate i.d. 0.4 mm. Three successive treatments with n-alkyl-dimethylsilanol using method b: 100 °C for 12 h, ammonia catalyst. Capillary rise method: average of 3 measurements; data marked with asterisk: points determined by two operators; average of 6 measurements.

a) Trimethylsiloxy layer[a])

x	0	10	20	30	40	50	60	70 °C
9	0.925	0.930	0.938	0.950	-	-	-	-
10	0.885	0.889	0.901	0.907	-	-	-	-
11	0.857	0.861	0.859	0.872	0.887	0.908	0.909	-
12	0.833	0.837	0.839	0.845	0.863	0.870	0.869	-
13	0.812	0.815	0.814	0.824	0.828	0.845	0.841	-
14		0.782	0.790	0.795	0.810	0.810	0.818	-
15			0.768	0.777	0.783	0.785	0.804	-
16			0.746	0.751	0.767	0.774	0.784	-
17				0.740	0.740	0.750	0.763	-
18				0.720	0.730	0.739	0.750	-
19					0.718	0.727	0.736	-
20					0.705	0.714	0.720	-

[a])Contact angles reveal that trimethylsiloxy surfaces are least reproducible of all. The cosines reported here are for the batch of capillaries which gave the lowest figures.

b) Ethyl-dimethylsiloxy layer

x	0	10	20	30	40	50	60	70 °C
9	1.000	1.000	1.000	1.000	-	-	-	-
10	0.971	0.976	0.980*	0.986*	0.991	0.996	0.997	-
11	0.943	0.949	0.952*	0.961*	0.967*	0.973*	0.978	0.990
12	0.922	0.930	0.919*	0.930*	0.947*	0.952*	0.954*	0.964
13	0.898	0.904	0.900*	0.910*	0.926*	0.932*	0.935*	0.946
14		0.869	0.885	0.889	0.902*	0.905*	0.915	0.920
15			0.858	0.868	0.871*	0.880*	0.889*	0.893
16			0.833*	0.844*	0.850*	0.864*	0.864*	0.873
17				0.825	0.827	0.841*	0.843*	-
18				0.810	0.816*	0.829*	0.836*	-
19					0.805	0.819	0.827	-
20					0.786	0.808*	0.817	-

25 °C: x = 16/cosθ = 0.841; 45 °C: 20/0.798; 65 °C: 16/0.865

c) Propyl-dimethylsiloxy layer

x	0	10	20	30	40	50	60	70 °C
9	1.000	1.000	1.000	1.000	-	-	-	-
10	0.982	0.987	0.984*	0.990*	0.998	0.999	1.000	-
11	0.963	0.958	0.951*	0.963*	0.996*	0.975*	0.990*	0.998
12	0.929	0.935	0.932*	0.943*	0.946*	0.954*	0.969*	0.970
13	0.910	0.914	0.911*	0.917*	0.924*	0.936*	0.940*	0.947
14		0.878	0.889	0.893*	0.902*	0.910*	0.916*	0.919
15			0.866	0.878	0.883*	0.887*	0.898*	-

c) Propyl-dimethylsiloxy layer (cont.)

x	0	10	20	30	40	50	60	70 °C
16			0.846*	0.853*	0.858*	0.875*	0.882*	0.886
17				0.838	0.840*	0.846*	0.862*	-
18				0.822*	0.825*	0.836*	0.847*	0.858
19					0.816	0.828	0.834	-
20					0.801*	0.809*	0.823	-

d) Hexyl-dimethylsiloxy layer

x	0	10	20	30	40	50	60	70 °C
9	1.000	1.000	1.000	1.000	-	-	-	-
10	0.994	0.996	0.988*	0.992*	0.994	0.992	0.991	0.993
11	0.971	0.975	0.970*	0.972*	0.972	0.979*	0.989*	0.993
12	0.955	0.958	0.953*	0.957*	0.959*	0.964*	0.972*	0.976
13	0.930	0.935	0.934*	0.936*	0.938*	0.944*	0.948*	0.954
14		0.902	0.909	0.912*	0.915*	0.918*	0.923*	0.925
15			0.891	0.892	0.896*	0.897*	0.906*	0.906
16			0.870*	0.874*	0.879*	0.882*	0.883*	0.882
17				0.860*	0.857*	0.866	0.869	-
18				0.838*	0.844*	0.843	0.846	0.845
19					0.834	0.835*	0.836*	-
20					0.820*	0.824*	0.824*	0.828

e) Decyl-dimethylsiloxy layer

x	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70 °C
9	0.989	-	0.993	-	0.994	-	1.000	-	-	-	-	-	-	-	-
10	0.980	-	0.985	-	0.982*	-	0.990*	-	0.994	-	0.997	-	0.997	-	-
11	0.968	-	0.972	-	0.961*	-	0.975*	-	0.974*	-	0.980*	-	0.986*	-	0.993
12	0.957	-	0.958	-	0.954*	0.964	0.964*	-	0.968*	-	0.972*	-	0.977*	-	0.980
13	0.949	-	0.948	-	0.943*	0.940	0.945*	0.947	0.950*	-	0.954*	-	0.957*	-	0.955
14			0.916	-	0.925*	0.927*	0.934*	0.932	0.934*	-	0.935*	-	0.941*	-	0.943
15				-	0.910	0.914*	0.918*	0.917	0.921*	0.921	0.919*	-	0.923*	-	0.926
16					0.905	0.905	0.906*	0.909	0.910*	0.911	0.910*	-	0.909*	-	0.920
17						-	0.891*	0.890	0.894*	0.894	0.897*	-	0.901*	-	0.901
18							0.878*	0.886	0.881*	0.885	0.885*	-	0.889*	-	0.895
19								0.876	0.871*	0.873	0.881*	-	0.888*	-	0.887
20									0.857	-	0.861*	-	0.861*	-	0.863

32.5 °C: x = 13/cosθ = 0.951, 14/0.929, 15/0.916, 16/0.909, 17/0.891, 18/0.878; 37.5 °C: 13/0.956, 14/0.929, 15/0.919, 16/0.909, 17/0.891, 18/0.886, 19/0.875; 42.5 °C: 15/0.918, 16/0.910, 17/0.891, 18/0.884, 19/0.870.

f) Tetradecyl-dimethylsiloxy layer

x	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70 °C
9	0.965	-	0.976	-	0.985*	-	0.996	-	-	-	-	-	-	-	-
10	0.927	0.944	0.953	0.964	0.973	0.978	0.978*	0.983	-	0.993	-	1.000	-	-	-
11	0.827	0.918	0.939	0.950	0.957	0.964	0.969	0.969	-	0.982	-	0.984	0.978	0.988	0.993
12	0.803	-	0.912	-	0.930*	0.938*	0.941*	0.948	0.951*	0.956	0.957*	0.967	0.963	0.970	0.974
13	0.784	0.836	0.902	0.915	0.918*	0.929*	0.921*	0.936*	0.933	0.955	0.940	0.954	0.948	0.964	0.970

f) Tetradecyl-dimethylsiloxy layer (cont.)

x	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70 °C
14			0.883	0.901	0.905*	0.911*	0.919*	0.922*	0.924	0.930	0.926	0.936	0.935	0.945	0.953
15					0.898	0.902*	0.908*	0.916*	0.916*	0.919*	0.919*	0.928	0.929*	0.938	0.940
16					0.890	0.905*	0.903*	0.911*	0.909*	0.913*	0.917*	0.914	0.918*	0.919	0.924
17							0.896*	0.900*	0.900*	0.902*	0.904*	0.906	0.909*	-	0.916
18							0.890	0.892*	0.891*	0.895*	0.895*	0.905	0.900*	0.911	0.903
19								0.885*	0.886*	0.890*	0.898*	0.900	0.901*	0.906	0.902
20									0.874*	0.874	0.881*	0.885	0.880*	0.889	0.879

2.5 °C: $x = 11/\cos\theta = 0.902$, 12/0.841, 13/0.809; 7.5 °C: 11/0.929, 12/0.889, 13/0.867; 12.5 °C: 11/0.943, 12/0.923, 13/0.904; 32.5 °C: 13/0.925, 14/0.919, 15/0.906, 16/0.907, 17/0.899, 18/0.885; 37.5 °C: 12/0.947, 13/0.940*, 14/0.921*, 15/0.915*, 16/0.911*, 17/0.899*, 18/0.892, 19/0.887; 42.5 °C: 13/0.953, 14/0.928, 15/0.920, 16/0.911, 17/0.900, 18/0.893*, 19/0.888*, 20/0.870; 47.5 °C: 12/0.961, 13/0.958, 14/0.928, 18/0.899; 52.5 °C: 18/0.903, 20/0.876; 62.5 °C: 18/0.904, 19/0.897, 20/0.881.

g) Octadecyl-dimethylsiloxy layer

x	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70 °C
9	0.970	-	0.981	-	0.991	-	1.000	-	-	-	-	-	-	-	-
10	0.928	0.933	0.953	0.961	0.969*	0.976	0.982*	0.985	-	0.991	-	0.997	-	-	-
11	0.876	0.883	0.884	0.894	0.924*	0.942	0.954*	0.960	0.968*	0.973	0.977	0.983	0.989	0.991	0.993
12	0.828	-	0.828*	-	0.832*	0.876*	0.923*	0.939	0.950*	0.954	0.963*	0.965	0.973	0.972	0.974
13	0.787	0.788	0.785*	0.788	0.791*	0.806*	0.819*	0.901*	0.929*	0.933	-	0.942	-	0.955	0.957
14			0.742*	0.755	0.751*	0.753*	0.757*	0.816*	0.882*	0.911	0.923*	0.925	0.938	0.933	0.942
15							0.743	0.752	0.820*	0.898*	0.907*	0.907	0.917*	0.917	0.921
16							0.734	0.736	0.797	0.882*	0.900*	0.899	0.910*	0.909	0.912
17							0.735	0.738	0.762	0.863*	0.889*	0.884	0.898*	0.887	0.894
18							0.738	0.748	0.775	0.872*	0.885*	0.888	0.894*	0.893	0.900
19									0.794	0.865*	0.885*	0.886	0.892*	0.891	0.895
20									0.813	0.874	0.884*	0.880	0.890*	0.886	0.887

22.5 °C: $x = 12/\cos\theta = 0.865$; 32.5 °C: 13/0.883, 14/0.762; 37.5 °C: 12/0.943, 13/0.920*, 14/0.851*, 15/0.782*, 16/0.739*, 17/0.742, 18/0.760, 19/0.790, 20/0.806; 42.5 °C: 12/0.952, 13/0.929, 14/0.905, 15/0.896, 16/0.840, 17/0.825, 18/0.832*, 19/0.813*, 20/0.842; 47.5 °C: 12/0.957, 13/0.935, 14/0.915, 18/0.871; 52.5 °C: 18/0.880, 19/0.879, 20/0.877

h) Docosyl-dimethylsiloxy layer

x	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70 °C
9	0.967	-	0.973	-	0.985	-	0.998	-	-	-	-	-	-	-	-
10	0.946	0.945	0.954	0.956	0.961*	0.967	0.974*	0.983	-	0.993	-	0.996	-	-	-
11	0.934	0.939	0.940	0.944	0.952*	0.955	0.960	0.967	-	0.978	0.981	0.987	0.992	0.995	0.998
12	0.914	-	0.913*	-	0.912*	0.918*	0.920*	0.932	0.948*	-	0.969*	0.971	0.978	0.982	0.987
13	0.882	0.879	0.873*	0.877	0.883	0.881	0.883	0.887	0.903	0.946	0.947	0.964	0.967	0.973	0.973
14			0.829*	0.832	0.835*	0.832*	0.836	0.841	-	0.868	0.905	0.929	0.937	0.939	0.946
15					0.786	0.789	0.788*	0.796	0.796	0.811	0.845	0.909	0.916*	0.923	0.929
16					0.743	0.748*	0.752	0.759	0.765	0.767	0.784	0.859	0.905*	0.915	0.923
17							0.711*	0.715*	0.716*	0.715*	0.719*	0.766	0.850*	0.892	0.906
18							0.692*	0.690	0.691	0.691	0.703*	0.726	0.786*	0.894	0.903
19								0.702	0.706	0.701	0.718	0.721	0.796	0.888	0.902
20									0.703	0.700	0.703	0.710	0.756	0.852	0.881

32.5 °C: $x = 17/\cos\theta = 0.714$, 18/0.689; 37.5 °C: 13/0.897, 14/0.838, 15/0.796, 16/0.757, 17/0.715*, 18/0.693, 19/0.704, 20/0.699; 42.5 °C: 12/0.955, 13/0.936, 14/0.854, 16/0.736, 17/0.714, 18/0.692, 19/0.705, 20/0.704; 47.5 °C: 12/0.960, 13/0.952, 14/0.893, 19/0.711, 20/0.697; 52.5 °C: 20/0.704; 62.5 °C: 19/0.847, 20/0.812.

the free energy difference caused by immerging a *dry* surface in the liquid; the free energy of immersion, ΔF_i^*, is measured by immerging a solid in equilibrium with the vapor of the wetting agent). The plots of the function $\Delta F_i^* = \gamma_{LV}\cos\theta$, *versus* temperature, demonstrated that in the absence of a 'surface melting anomaly' the points for different alkanes did not show a significant deviation from linearity. Furthermore, all lines were parallel for a given surface. Therefore, for ΔF_i^* on the surfaces treated with methyl-, ethyl-, hexyl-, decyl- and tetradecyl-dimethylsilanol the following family of equations was calculated using the method of least squares

$$\Delta F_i^*(z) = \Delta F_i^{*,0}(z) - \Delta s_i^* \ (T - 273.16) \tag{32}$$

where T is the absolute temperature, and Δs_i^* is the immersion entropy.

For the heats of immersion on surfaces treated with octadecyl- and docosyl-dimethylsilanol the parameters of the following equation were first estimated from the plot of ΔF_i^* *versus* temperature:

$$\Delta F_i^*(z) = \Delta F_i^{*,0}(z) - \Delta s_i^* \ (T - 273.16) + \Delta h_{i,tr}^* \ (z) \int_{-\infty}^{T} (\sigma_{tr}^2 \pi)^{-1/2} \exp[-(T - T_{tr})^2/\sigma_{tr}^2] dT \tag{33}$$

where $\Delta h_{i,tr}^*$ is the transition enthalpy, T_{tr} is the transition temperature and σ_{tr} is the standard deviation of the error function around T_{tr}. Then, with the aid of a computer, the sum of the squares of the deviations, $\Sigma\delta^2 = \Sigma(\Delta F_i^*(z)_{regr.} - \Delta F_i^*(z)_{exp.})^2$ was minimized following a complete factorial design on three levels for each of the parameters $\Delta F_i^{*,0}$, $\Delta h_{i,tr}^*(z)$, T_{tr} and σ_{tr}. Again it was supposed that Δs_i^*, is independent of z. The results are summarized in *Tables 8* and *9*. Obviously, the analogous enthalpy of immersion can be calculated from

$$\Delta h_i^* = \Delta F_i^* - \frac{\partial \Delta F_i^*}{\partial T} T = \Delta F_i^{*,0} - 273.16 \ \Delta s_i^* \tag{34}$$

Therefore, in *Table 8* the term (273.16 Δs_i^*) is also given.

Approximation of Eq. (12) *and* (19) *in the space* $\cos\theta$ versus γ_{LV}^a *using linear regression (see 2.4).* The problem is to approximate Eq. (12) and (19) by linear function, between the limits: $\cos\theta = y_0$ and $\cos\theta = 1$ to give Eq. (24) with a slope, b, and an intersection with $\cos\theta = 1$, designated as γ_c. In order to find this linear function, we use the method of least squares, which, in the continuous case consists in finding the values of b and γ_c which minimize the integral

$$I = \int_{y_0}^{1} [\gamma_{LV}^a(\cos\theta) - (\cos\theta - 1)/b - \gamma_c]^2 d\cos\theta \tag{35}$$

where $\gamma_{LV}^a = \gamma_{LV}^a(\cos\theta)$ is given by Eq. (12) or (19). This means resolving the system of Eq. (36):

$$\left.\begin{aligned} 0 &= \int_{y_0}^{1} \frac{\partial}{\partial b} [\gamma_{LV}^a(\cos\theta) - (\cos\theta - 1)/b - \gamma_c]^2 d\cos\theta \\ &\text{and} \\ 0 &= \int_{y_0}^{1} \frac{\partial}{\partial \gamma_c} [\gamma_{LV}^a(\cos\theta - (\cos\theta - 1)/b - \gamma_c]^2 d\cos\theta \end{aligned}\right\} \tag{36}$$

The solution gives

$$\gamma_c = 2(1 - y_0)^{-2} [3B - (1 + 2y_0)A] \tag{37}$$

$$b = (1 - y_0)^3 [12B - 6(1 + y_0)A]^{-1} \tag{38}$$

where the values of A and B are given by the definite integrals

$$\left.\begin{aligned} A &= \int_{y_0}^{1} \gamma_{LV}^a(\cos\theta) d\cos\theta \\ &\text{and} \\ B &= \int_{y_0}^{1} \cos\theta \, \gamma_{LV}^a(\cos\theta) d\cos\theta \end{aligned}\right\} \tag{39}$$

Table 8. *Free energy of immersion at 0°C of the alkyl-dimethylsiloxy surface saturated with the vapor of the wetting agent.* The mean entropy of immersion, Δs_i^*, and the mean enthalpy of immersion, Δh_i^*, is also listed. Enthalpies and free energies are in erg cm^{-2} (=mJm^{-2}) entropies are in erg cm^{-2} degree^{-1}. To find enthalpies, add 273.16× Δs_i^*. To obtain values in mcalm^{-2}, multiply by 0.239. The experimental error is, in general less than ±0.1 for the free energies, ±0.002 for the entropy and consequently, ±0.6 for enthalpies. Values in italics are relative values, referred to the trimethylsiloxy surface.

Wetting alkane	Substituent									
	Methyl	Ethyl	Propyl	Hexyl	Decyl	Tetradecyl	Octadecyl		Docosyl	
							below trans. temp.	above	below trans. temp.	above
Undecane	−22.4	−24.6	−24.8	−25.4	−25.3	−24.7	−23.2	−24.5		−24.7
	1	*1.098*	*1.107*	*1.134*	*1.129*	*1.102*	*1.036*	*1.094*		*1.103*
Dodecane	−22.4	−24.7	−25.0	−25.7	−25.8	−25.0	−22.4	−24.9	−24.5	−24.9
	1	*1.103*	*1.116*	*1.147*	*1.152*	*1.116*	*1.000*	*1.112*	*1.094*	*1.112*
Tridecane	−22.3	−24.8	−25.1	−25.8	−26.0	−25.4	−21.8	−25.1	−24.2	−25.5
	1	*1.112*	*1.126*	*1.157*	*1.166*	*1.139*	*0.978*	*1.126*	*1.085*	*1.143*
Tetradecane	−22.0	−24.8	−24.9	−25.7	−26.1	−25.5	−21.2	−25.3	−23.3	−25.3
	1	*1.127*	*1.132*	*1.168*	*1.186*	*1.159*	*0.964*	*1.150*	*1.059*	*1.150*
Pentadecane	−21.9	−24.6	−24.9	−25.7	−26.2	−25.8	−21.4	−25.4	−22.6	−25.4
	1	*1.123*	*1.136*	*1.174*	*1.196*	*1.178*	*0.977*	*1.160*	*1.032*	*1.160*
Hexadecane	−21.8	−24.4	−24.8	−25.6	−26.4	−26.0	−21.4	−25.6	−21.9	−25.7
	1	*1.119*	*1.138*	*1.174*	*1.211*	*1.193*	*0.982*	*1.174*	*1.005*	*1.179*
Heptadecane	−21.7	−24.3	−24.7	−25.6	−26.4	−26.2	−21.8	−25.6	−21.2	−25.7
	1	*1.120*	*1.138*	*1.180*	*1.217*	*1.207*	*1.005*	*1.180*	*0.977*	*1.184*
Octadecane	−21.6	−24.3	−24.8	−25.4	−26.5	−26.3	−22.3	−26.0	−20.8	−26.3
	1	*1.125*	*1.148*	*1.176*	*1.227*	*1.218*	*1.032*	*1.204*	*0.963*	*1.213*
Nonadecane	−21.6	−24.4	−24.8	−25.5	−26.6	−26.5	−23.8	−26.2	−21.4	−26.3
	1	*1.130*	*1.148*	*1.181*	*1.231*	*1.227*	*1.102*	*1.213*	*0.991*	*1.213*
Eicosane	−21.4	−24.3	−24.6	−25.5	−26.4	−26.3	−24.4	−26.4	−21.6	−26.2
	1	*1.135*	*1.150*	*1.192*	*1.234*	*1.229*	*1.140*	*1.234*	*1.009*	*1.224*
Δs^*	−0.052	−0.062	−0.064	−0.074	−0.074	−0.064	−0.063		−0.061	
	1	*1.19*	*1.23*	*1.42*	*1.42*	*1.23*	*1.21*		*1.17*	
Average $\Delta F_i^{*,0}$	−21.9	−24.5	−24.8	25.6	26.2	25.8	–	25.5	–	25.6
	1	*1.119*	*1.134*	*1.168*	*1.195*	*1.177*	–	*1.165*	–	*1.168*
273.16× Δs_i^*	14.2	16.9	17.5	20.2	20.2	17.5	–	17.2	–	16.7
Average Δh_i^*	−36.1	−41.4	−42.3	−45.8	−46.4	−43.3	–	−42.7	–	−42.3

Table 9. *Transition temperatures,* T_{tr}, *of the mixed surface crystals on octadecyl- and docosyl-dimethylsiloxy surfaces.* The standard deviation of the transition temperature domain, σ_{tr}, as well as the change of the enthalpy, $\Delta h^*_{i,tr}$, and entropy of immersion, $\Delta s^*_{i,tr}$ $(=\Delta h^*_{i,tr}/T_{tr})$ are given.

Wetting agent	Octadecyl				Docosyl			
	T_{tr} °C	σ_{tr} °C	$\Delta h^*_{i,tr}$ erg cm^{-2}	$\Delta s^*_{i,tr}$ erg cm^{-2} degree^{-1}	T_{tr} °C	σ_{tr} °C	$\Delta h_{i,tr}$ erg cm^{-2}	$\Delta s^*_{i,tr}$ erg cm^{-2} degree^{-1}
Undecane	18.9	4.9	-1.3	$-4.5\cdot10^{-3}$	~25		~-0.2	$-0.7\cdot10^{-3}$
Dodecane	25.8	4.8	-2.5	$-8.4\cdot10^{-3}$	38.8	3.7	-0.5	$-1.6\cdot10^{-3}$
Tridecane	32.1	4.1	-3.3	$-10.8\cdot10^{-3}$	41.1	4.1	-1.3	$-4.1\cdot10^{-3}$
Tetradecane	36.6	3.9	-4.1	$-13.2\cdot10^{-3}$	47.0	4.3	-1.9	$-5.9\cdot10^{-3}$
Pentadecane	39.6	3.2	-4.0	$-12.8\cdot10^{-3}$	50.3	3.8	-2.8	$-8.7\cdot10^{-3}$
Hexadecane	41.1	3.4	-4.2	$-13.4\cdot10^{-3}$	53.4	4.9	-3.8	$-11.6\cdot10^{-3}$
Heptadecane	42.0	2.2	-3.8	$-12.1\cdot10^{-3}$	57.4	4.1	-4.5	$-13.6\cdot10^{-3}$
Octadecane	41.5	3.3	-3.7	$-11.8\cdot10^{-3}$	60.1	4.9	-5.5	$-16.5\cdot10^{-3}$
Nonadecane	43.6	1.9	-2.4	$-7.6\cdot10^{-3}$	59.8	5.0	-4.9	$-14.7\cdot10^{-3}$
Eicosane	42.3	2.2	-1.9	$-6.0\cdot10^{-3}$	62.1	3.9	-4.6	$-13.7\cdot10^{-3}$

Defining

and

$$\left.\begin{aligned} w&=(1-y_0)/\psi \\ p&=-\gamma_c b/(1-y_0) \end{aligned}\right\} \tag{40}$$

the product, wp, can be approximated with a good precision, by the first three members of its *Taylor* series expanded around $w=0$ (*i.e.* $y_0=1$). The approximation for p is then after rearrangement:

Fowkes
$$p \approx 1/w - 3/4 - w/80 \tag{41}$$

Zettlemoyer
$$p \approx 1/w - 1 - w/15 \tag{42}$$

It can easily be shown with the aid of Eq. (39) that γ_c is proportional to $\gamma^d_{S,obs}$. Consequently, in the knowledge of w (presuming the knowledge of y_0 and ψ) it is possible to calculate the ratio, $\gamma^d_{S,obs}/\gamma_c=\phi$, as defined by Eq. (28):

Fowkes
$$\phi(w)=w^2[24\ln(1-2/w)-8w(3-w)/(2-w)]^{-1} \tag{43}$$

Zettlemoyer
$$\phi(w)=w^2[6w+(6-4w)\ln(1-w)]^{-1}. \tag{44}$$

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