

Wetting of low energy model surfaces

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Abstract - Cosines of contact angles of liquid paraffins found on a surface, S, gave a linear plot as a function of cosines of contact angles of the same paraffins measured on a non-polar, standard surface, D. Slope and intercept of the resulting linear regression could be interpreted in terms of areal surface free energy, surface roughness and swelling capacity. The standard surface as well as model surfaces were prepared by chemically bonding triorganylsiloxo grafts on silica and acid leached glass. It was shown that the method can be also applied to the interpretation of liquid/liquid contact systems.

INTRODUCTION

No method is known for the determination of areal surface free energy of solids, an analogous quantity to the surface tension of liquids. Methods for its estimation are based on the interpretation of contact angles between wetting agents of known surface tension and the solid to be characterized. Following Zisman's proposal (ref. 1) cosines of contact angles are plotted as a function of the surface tension of the wetting liquid. A regular pattern appears especially if paraffins are used as wetting agents suggesting that liquids of low surface tension wet better. Extrapolation of the correlation to $\cos\theta = 1$, gives a "critical surface tension, γ_c " which is the surface tension of a hypothetical paraffin just low enough to spread and form a film at the solid surface. Girifalco and Good applied a semiempirical approach (refs 2 & 3). The energy between two liquids in contact is supposed to follow Berthelot's rule (ref. 4). Thus, it can be calculated as the geometric mean of the energies acting between molecules of the pure liquids. Consequently, the interfacial tension may be calculated from the surface tension of the liquids in contact. Fowkes proposed that these calculations are strictly valid only for that part of interaction forces which is due to dispersion forces (refs 5 & 6). Therefore, the cosine of the contact angle should be linear function of $\sqrt{\gamma_\ell^{(d)}/\gamma_\ell}$ where $\gamma_\ell^{(d)}$ is the "dispersion part" of the surface tension of the liquid, ℓ . The slope of the resulting plot permits the calculation of γ_c .

THE STANDARD SURFACE METHOD

In the following a new approach is presented based on the comparison of contact angles measured on the surface S with those found on a standard surface, capable of interaction with any sort of wetting agent by dispersion forces only (ref. 7).

The starting quantity is the free energy of adhesion (ref. 3)

$$-\Delta f_{1,2} = \gamma_1 + \gamma_2 - \gamma_{1,2} \quad (1)$$

where γ_1 and γ_2 are the surface tensions of the contacting liquids and $\gamma_{1,2}$ is the interfacial tension. Supposing that eqn 1 is also valid for the solid/liquid couple the free energy of adhesion can be determined experimentally from contact angle measurement.

From Young's equation

$$\gamma_\ell \cos\theta_{S,\ell} = \gamma_S - \gamma_{S,\ell} - \pi \quad (2)$$

the sum of two unknowns, the areal free energy of the surface, γ_S , and the interfacial tension between the solid and the wetting agent, $\gamma_{S,\ell}$, is measured. By supposing that the surface pressure, π , is negligible the free energy of adhesion is calculated by simple extension of eqn 2.

$$-\Delta f_{S,\ell} = \gamma_S + \gamma_\ell - \gamma_{S,\ell} = \gamma_\ell (\cos\theta_{S,\ell} + 1) \quad (3)$$

Let us follow the idea of Hildebrand and Scott (ref. 8) for the calculation of interaction forces between molecules in liquid mixtures as proposed by Fowkes (refs 6, 9 & 10). By ana-

logy, it will be assumed that the interaction potential (in the sense of capability) of a solid and a liquid surface across the interface is given by a series of constants

$$S : \vec{\delta}_S = (\delta_S^{(d)}, \delta_S^{(p)}, \delta_S^{(Ha)}, \delta_S^{(Hd)}, \dots) ; \ell : \vec{\delta}_\ell = (\delta_\ell^{(d)}, \delta_\ell^{(p)}, \delta_\ell^{(Ha)}, \delta_\ell^{(Hd)}, \dots) \quad (4)$$

where the superscripts d, p, Ha, Hd, ... refer to interactions by dispersion forces, polar forces, hydrogen bridge formation as proton acceptor and donor, etc. The list of δ -s can be extended. The dimension of the interaction potentials is $\sqrt{\text{energy/area}}$. It is now assumed that the interaction vector, $\vec{\delta}$, is a property of the surface S and of the liquid ℓ , and is independent of the contact partner. The free energy of adhesion is then given by

$$-\Delta f_{S,\ell} = 2d \delta_S^{(d)} \delta_\ell^{(d)} + 2p \delta_S^{(p)} \delta_\ell^{(p)} + \dots \quad (5)$$

where the constants d, p, ... are interaction coefficients independent of S and ℓ .

Molecules of liquid paraffins attract each other nearly exclusively by dispersion forces, so they can be considered as non-polar liquids (ref. 11). Let us now suppose that there exists also a standard surface, D, which can only interact by dispersion forces. The adhesion energy of paraffins on the surface D and S is then given by

$$\text{Surface D} \quad -\Delta f_{D,\text{par}} = 2d \delta_D \delta_{\text{par}} = \gamma_{\text{par}} (\cos\theta_{D,\text{par}} + 1) \quad (6)$$

$$\text{Surface S} \quad -\Delta f_{S,\text{par}} = 2d \delta_S^{(d)} \delta_{\text{par}} = \gamma_{\text{par}} (\cos\theta_{S,\text{par}} + 1) \quad (7)$$

Combination of eqns 6 and 7 gives

$$(\cos\theta_{S,\text{par}} + 1) = \sqrt{D_S} (\cos\theta_{D,\text{par}} + 1) \quad (8)$$

where the ratio

$$D_S = (\delta_S^{(d)} / \delta_D)^2 \quad (9)$$

is interpreted as the relative areal surface free energy of the solid S, due to dispersion forces. By plotting $(\cos\theta_{S,\text{par}} + 1)$ as a function of the same function of the paraffin contact angles determined on surface D, the points fall on a straight line of slope $\sqrt{D_S}$. The line has an intercept of zero.

The method can be extended to rough and to swellable surfaces. On rough surfaces, eqn 10 holds (ref. 12)

$$-\Delta f_{S,\ell}^{(r)} = r\gamma_S + \gamma_\ell - r\gamma_{S,\ell} = \gamma_\ell (\cos\theta_{S,\ell} + 1) \quad (10)$$

where r, the roughness is the real surface area of a projected unit surface area. Obviously $r \geq 1$. Combination of eqns 6, 7 and 10 results, for paraffins, in the following expression :

$$(\cos\theta_{S,\text{par}}^{(r)} + 1) = (1-r) + r\sqrt{D_S} (\cos\theta_{D,\text{par}} + 1) \quad (11)$$

The analogous relationship for swollen surfaces is derived as follows. Following the proposal of refs 13 and 14 the free energy of adhesion of the liquid, ℓ , with a heterogeneous surface, h, composed of patches of S1 and S2 is given as the linear combination of eqn 12

$$\Delta f_S^{(h)} = \alpha \Delta f_{S1} + (1 - \alpha) \Delta f_{S2} \quad (12)$$

where α is the fraction of the surface of the type S1. On a swollen surface the wetting agent is in contact only with a fraction α of the solid S; on the fraction $(1 - \alpha)$ the wetting agent is in contact with itself. On the latter, impregnated fraction, $\cos\theta = 1$. Combination of eqns 6, 7 and 12 gives for paraffins

$$(\cos\theta_{S,\text{par}}^{(\text{sw})} + 1) = 2(1 - \alpha) + \alpha\sqrt{D_S} (\cos\theta_{D,\text{par}} + 1) \quad (13)$$

The percentage $100(1 - \alpha)$ is called the swelling capacity. Eqns 8, 11 and 13 can be summarized as follows. By plotting $(\cos\theta_{S,\text{par}} + 1)$ as a function of $(\cos\theta_{D,\text{par}} + 1)$ a linear plot is obtained. If its intercept at zero is positive, intercept and slope will be interpreted as those on a swollen surface (eqn 13). If the intercept is negative the surface S will be considered to be rough (eqn 11).

MODEL SURFACES

Low energy surfaces were prepared by the reaction of triorganyl(dimethylamino)silanes with acid leached glass capillaries at 180°C for 100 h. This reaction is known to give densest monolayers on surface hydrated silica (ref. 15). Only circumstantial evidence can be given that this is also the case on acid leached glass. Actually, capillaries treated at conditions which on silica did not give dense layers, showed higher contact angles (ref. 16).

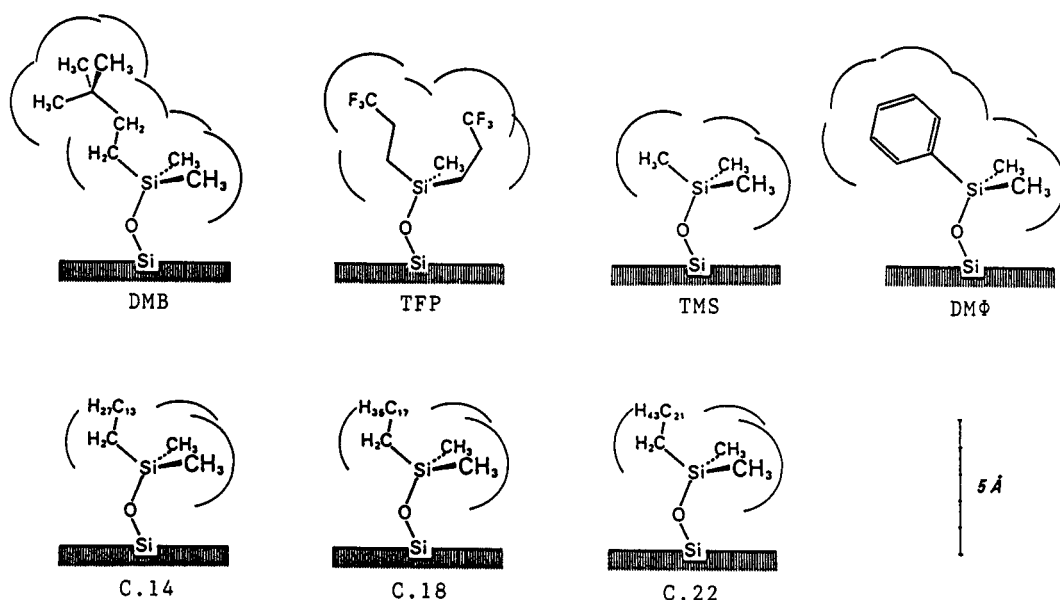


Fig. 1. The structure of the triorganylsiloxy substituents.

The surface covered by a dense monolayer of the (3,3-dimethylbutyl)dimethylsiloxy, DMB, substituent was chosen as the standard surface ($\Gamma_{\text{SOX}} = 3.86 \mu\text{mol m}^{-2}$ on silica (ref. 15)). In fact this bulky, non-polar substituent doubly shields the surface. The bis(trifluoropropyl) methylsiloxy, TFP, covered surface ($\Gamma_{\text{SOX}} = 3.14 \mu\text{mol m}^{-2}$) was chosen as an example of a polar surface. The trimethylsiloxy, TMS, covered surface ($\Gamma_{\text{SOX}} = 4.72 \mu\text{mol m}^{-2}$) will be shown to be slightly polar. The phenyldimethylsiloxy, DMφ, covered surface ($\Gamma_{\text{SOX}} = 4.18 \mu\text{mol m}^{-2}$) was expected to have a high areal surface free energy. As examples of swellable surfaces tetradecyldimethylsiloxy and octadecyldimethylsiloxy and docosyldimethylsiloxy, C.14, C.18 and C.22 covered capillaries were prepared ($\Gamma_{\text{SOX}} = 4.2 \mu\text{mol m}^{-2}$). With the aid of the silylated capillaries contact angles could be determined in a thermostated vessel up to 200°C by the method of capillary rise. Surface tension and density of some 80 wetting agents are from ref. 17. In the usual experimental temperature range of 20–80°C the reproducibility of the $\cos\theta$ was in the order of ± 0.002 .

DATA ON THE DMB-COVERED STANDARD SURFACE

The areal surface free energy of the DMB-covered surface, chosen as standard, cannot be determined; furthermore, in the light of the preceding section it will depend on the nature of its contact partner. A quantity analogous to the critical surface tension can be determined as follows. In Fig. 2 the plot of $\ln(\cos\theta_{\text{D,par}} + 1)$ is shown as a function of the logarithm of the surface tension of the wetting paraffin, $\ln\gamma_{\text{par}}$. The value of $\ln\gamma_{\text{par}}$ at the intercept of the regression equation with $\ln(\cos\theta_{\text{D,par}} + 1) = \ln 2$ is the highest surface tension of a paraffin just wetting the standard surface. This is certainly a property of the surface but is given in terms of an equivalent surface tension of a liquid. For this paraffin eqn 6 simplifies to give

$$\delta_{\text{D}} \delta_{\text{led}}^{\dagger} = \gamma_{\text{led}}^{\dagger} \quad (14)$$

where $\gamma_{\text{led}}^{\dagger}$ is the "liquid equivalent of the dispersion part" of the areal free surface energy of the standard solid (ref. 7). By putting $d = 1$ and $\sqrt{\gamma_{\text{led}}^{\dagger}} = \delta_{\text{led}}^{\dagger}$ we get

$$(\delta_{\text{D}})^2 = \gamma_{\text{led}}^{\dagger} \quad (15)$$

By accepting $\gamma_{\text{led}}^{\dagger}$ as the (surface tension equivalent of the) areal surface free energy of the standard D, the analogous free energy of any surface S can be calculated if DS is known.

$$\gamma_{\text{led,S}} = D_{\text{S}} \gamma_{\text{led}}^{\dagger} \quad (16)$$

Fig. 2 shows the plot of $\ln(\cos\theta_{\text{D,par}} + 1)$ of 24 paraffins measured on the standard surface as a function of the logarithm of the surface tension of the paraffin, γ_{par} , at different temperatures. The liquid equivalent of the surface energy is given, between 20–80°C, by

$$\gamma_{\text{led}}^{\dagger} = 23.90 - 0.0684 (T - 273.15) \text{ erg cm}^{-2} \quad (17)$$

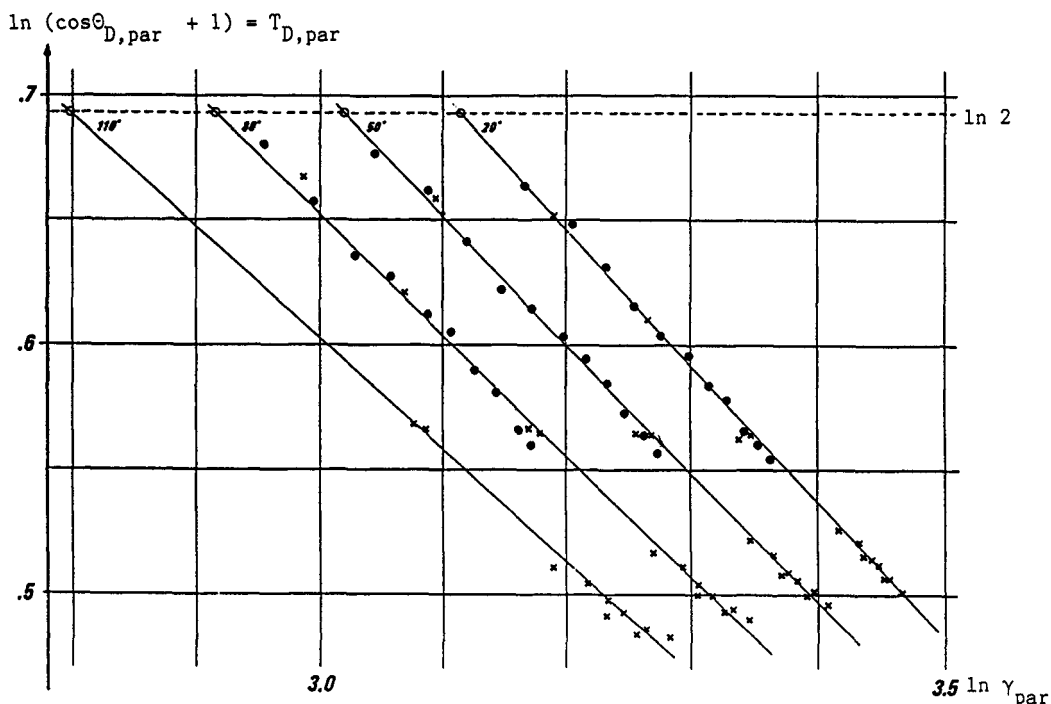


Fig. 2. Wetting of the DMB-covered standard non-polar surface by paraffins; plot of $\ln(\cos\theta_{D,par} + 1) = T_{D,par}$ as a function of the surface tension of the wetting paraffin (logarithmic scale, $\ln \gamma_{par}$). The γ_{led}^\dagger is found at the intercept with the horizontal at $\ln 2$ (open circles).

With the aid of 10 branched paraffins of low volatility, the same property was determined between 20–200°C to give the empirical relationship

$$\gamma_{led}^\dagger = 43.3 [1 - (T/741.5)]^{4/3} \text{ erg cm}^{-2} \quad (18)$$

The absolute value of γ_{led} calculated with eqn 18 is systematically lower than that given by eqn 17 due to small differences between the wetting behaviour of paraffins. However, it is very interesting to note that the temperature dependence of γ_{led}^\dagger is described by the same type of relationship as that proposed for the surface tension of a liquid (an exponent of 1.21 is proposed in refs 18 and 19; see also ref. 20).

On this same surface the free energy of adhesion was now determined for some 80 liquids in the temperature domain of 20–80°C. The liquids included normal and branched paraffins, cycloalkanes, chloro- bromo- nitro- cyano-alkanes and aromatics, alcohols, water, mercury and some miscellaneous liquids. The value of $-\Delta f_{D,\ell}$ at 20°C was tabulated together with the corresponding entropy, $\Delta s_{D,\ell}$ (ref. 7).

WETTING OF MODEL SURFACES

In Fig. 3 the plot of $(\cos\theta_{S,\ell} + 1)$ is shown as a function of $T_{D,\ell} = (\cos\theta_{D,\ell} + 1)$ at 20 and 80°C, on the TFP-covered glass, a surface of relatively high polarity. On the regression line are the points of all paraffins and that of mercury which behaves in contact with low energy surfaces as a non-polar wetting agent. All polar wetting agents are above the regression line as suggested by eqn 5. The slope of the correlation line is practically independent of the temperature. The regression was calculated with the points for paraffins only and despite of the large extrapolation, the intercept at the origin does not deviate significantly from zero.

As is seen from the plot of Fig. 4, the TMS-covered surface is slightly polar as was also noted by Zettlemoyer (ref. 21). Obviously, the deviation of a polar liquid from the regression line of the nonpolar liquids is proportional to the polarity of the surface (more efficient wetting). From the deviation of about 50 polar wetting agents a relative polarity of about 7% was calculated for the TMS-covered surface, relative to the polarity of the TFP-graft.

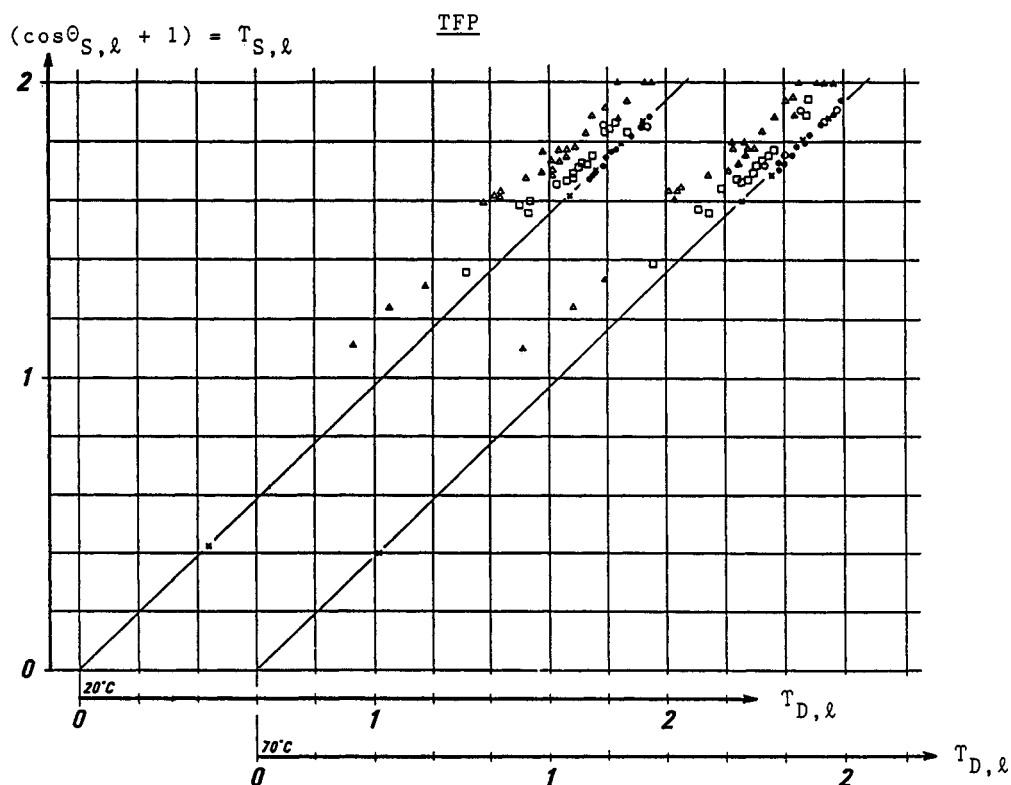


Fig. 3. Wetting properties of the TFP-covered surface. Symbols : n-alkanes : ● ; branched alkanes and mercury : * ; polar type compounds with no dipole moment : ○ ; polar compounds with hydroxyl groups : ▲ ; polar compounds with H-acceptor group : △ ; other polar wetting agents : □ .

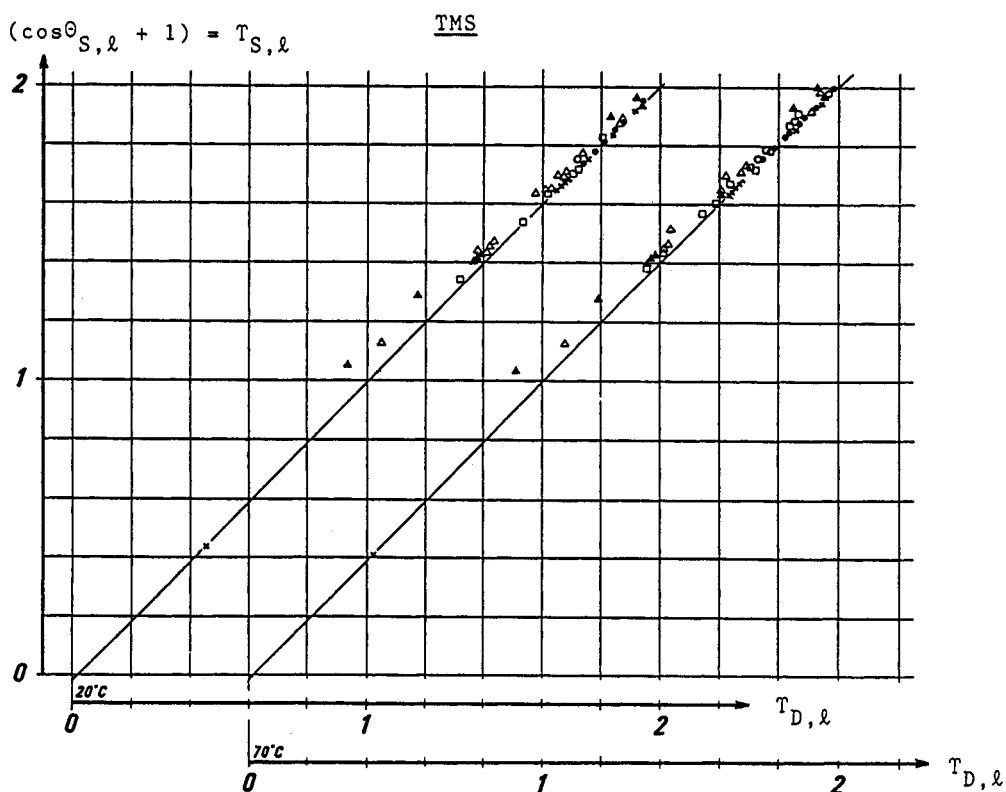


Fig. 4. Wetting properties of the TMS-covered surface. For symbols see caption to Fig. 3.

In Fig. 5 the plot of wetting of the C.14-covered surface is shown for an example of a graft which can be swollen by some wetting agents. The C.14 chain being non-polar, the surface will be swollen by non-polar liquids. The slope of the corresponding regression line corresponds to a swelling capacity of 34 %. In addition to swelling, an interesting wetting anomaly is observed on the C.18 and C.22 grafts. If wetted by non-branched alkanes (but also by other rod-like wetting agents) a low energy layer is formed by cocrystallization of the alkyl chains of the graft and of the wetting alkane. Fig. 6 shows the wetting behaviour of a few chosen liquids as a function of the temperature (refs 7 & 16).

Results obtained on grafts of substituents shown in Fig. 1 are summarized in Table I.

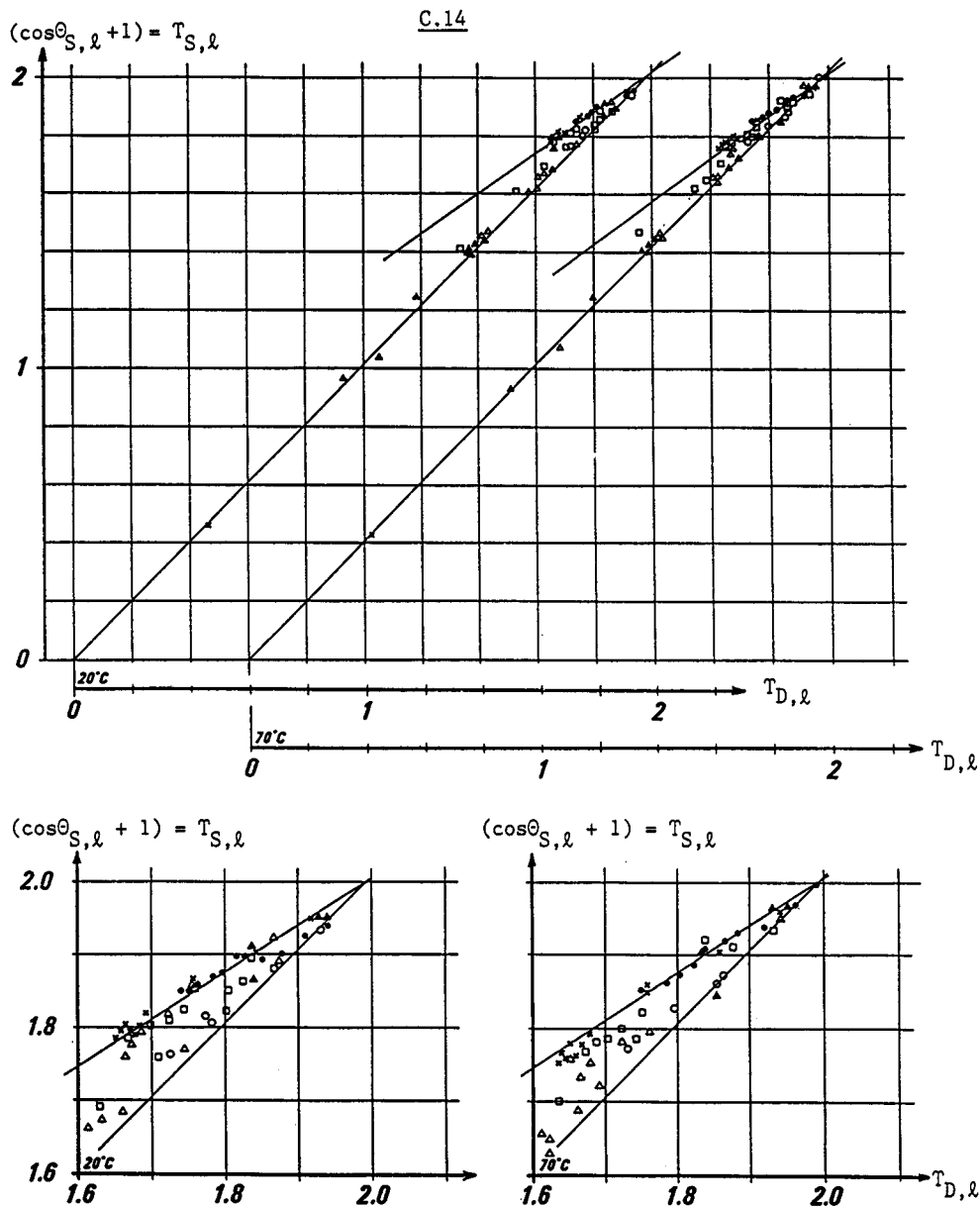


Fig. 5. Wetting properties of the C.14-covered surface. For symbols see Fig. 3.

TABLE I. Properties of dense grafts of substituents depicted in Fig. 1

Surface :	DMB	TFP	TMS	DM Φ	C.14	C.18	C.22	
Swelling cap.	0	0	0	0	34	45	51	%
D _S	$\frac{1}{2}$	0.938	0.993	1.414	1.01	1.04	1.06	
P _S	$\frac{0}{2}$	$\frac{1}{2}$	0.07	0.50	0.0	0.0	0.0	
$\gamma_{led,S}(20^\circ\text{C})$	22.54	21.14	22.38	31.87	22.8	23.5	24.0	dyn cm ⁻¹

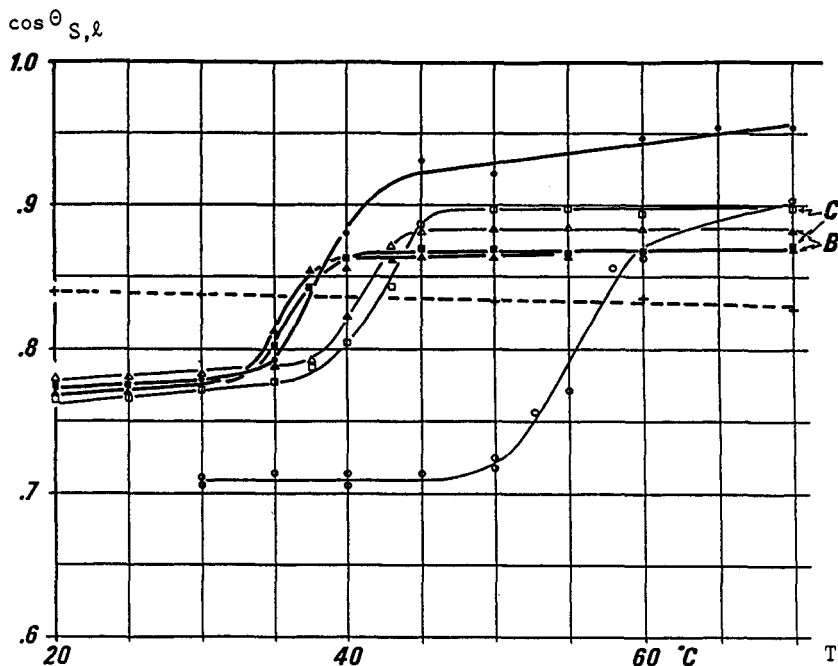


Fig. 6. Examples of anomalous wetting. Full symbols refer to data on the C.18-covered surface, open symbols to those measured on the C.22-covered surface. The broken line indicates a normal wetting behaviour : a branched C₅₉-paraffin on the C.18-covered surface. n-Alkanes : tridecane on C.18 and heptadecane on C.22. Curve B : 1-bromohexadecane; curve C : 1-chlorohexadecane.

MERCURY AND WATER

In Fig. 7, the plot of fictive $T_{X,l} = (\cos\theta_{X,l} + 1)$ values on water and mercury is shown as a function of $T_{D,l} = (\cos\theta_{D,l} + 1)$. They were calculated from surface tension and interfacial tension data of the contact partners with eqn 19 (refs 22, 23 & 24).

$$T_{X,l} = "(\cos\theta_{X,l} + 1)" = (\gamma_X + \gamma_l - \gamma_{X,l}) / \gamma_l \quad (19)$$

where X = water or mercury. Obviously T_l can be higher than 2. The plot of Fig. 7 suggests that the method presented could also describe interfacial properties of liquid/liquid couples.

TABLE II. Evaluation of surface properties of water and mercury by the standard surface method.

Surface :	Water	Mercury	
D _S	0.939	9.16	
P _S	9.16	0.0	
$\gamma_{led,X}$	21.2 ± 0.3	205 ± 5	dyn cm ⁻¹

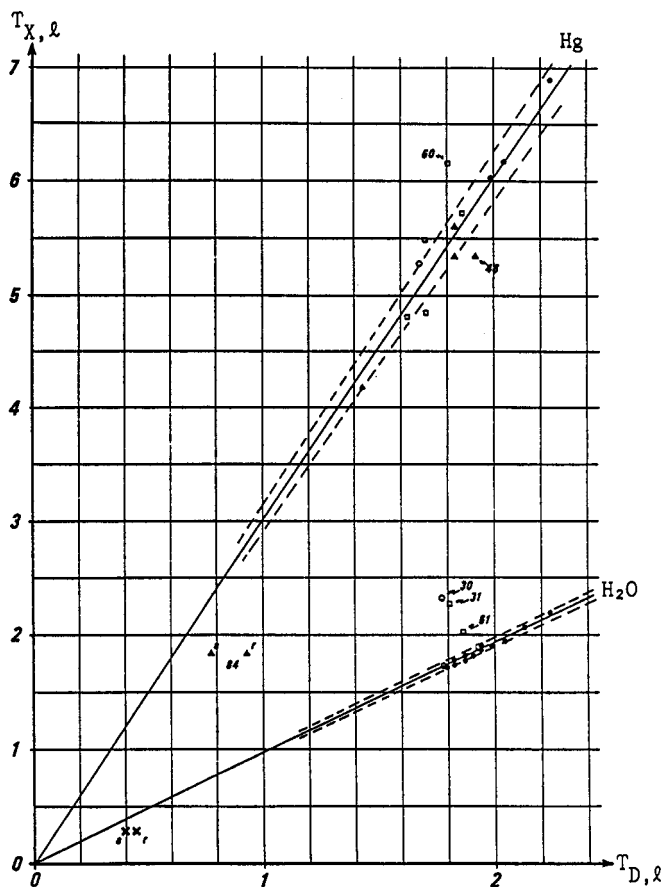


Fig. 7. Wetting properties of mercury and water at 20°C. For details see text. Full circles : n-alkanes; No 30 : benzene; 31 : toluene; 46 : methanol; 60 : dichloromethane; 61 : tetrachloromethane; 84 : water; 85 : mercury.

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