



ELSEVIER

Colloids and Surfaces
A: Physicochemical and Engineering Aspects 142 (1998) 219–235

COLLOIDS
AND
SURFACES

A

Measuring and interpreting contact angles: a complex issue

D.Y. Kwok, C.N.C. Lam, A. Li, A. Leung, R. Wu, E. Mok, A.W. Neumann *

*Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road,
Toronto, Ontario, Canada M5S 3G8*

Received 27 November 1997; accepted 27 January 1998

Abstract

Low-rate dynamic contact angles of 30 liquids on a FC-725-coated wafer surface were measured by an automated axisymmetric drop shape analysis-profile (ADSA-P). Surprisingly, results indicate that FC-725 behaves differently in some respects from what one would expect for non-polar surfaces: only nine liquids yield essentially constant contact angles whereas the others show slip/stick contact angle behaviour. In the worst case, the contact angle increases from ca 50 to 160° at essentially constant three-phase contact radius. These angles should be disregarded for the interpretation in terms of surface energetics since there is no guarantee that Young's equation is applicable. If one employs a conventional goniometer-sessile drop technique, such contact angle behaviour cannot be easily seen in all cases. These results indicate that the claim from van Oss et al. [Langmuir 4 (1988) 884] that liquids with the same contact angles do not have the same surface tensions is misleading. If the meaningful contact angles are plotted as the liquid–vapour surface tension times cosine of the contact angle versus the liquid–vapour surface tension, that is, $\gamma_{lv} \cos \theta$ versus γ_{lv} , a smooth curve emerges. Thus, intermolecular forces (or surface tension components) do not have an additional and independent effect on the contact angles, in good agreement with the results from other studies on non-polar and polar polymers. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Contact angle, dynamic; Contact angle, complexity; Solid surface tension, from contact angle; Solid surface tension, equation of state

1. Introduction

Young's equation is an important relation since it interrelates the Young contact angle, θ_Y , liquid–vapour surface tension, γ_{lv} , solid–vapour surface tension, γ_{sv} , and solid–liquid surface tension, γ_{sl} :

$$\gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl} \quad (1)$$

Because γ_{sv} and γ_{sl} are not directly measurable, Eq. (1) provides a possibility for the determination of these tensions only when an additional equation

involving the three interfacial tensions is known. Several approaches [1–8], of current interest, were largely inspired by this idea in pursuit of the determination of solid surface tensions from contact angles.

Eq. (1) stipulates a single, unique contact angle; in practice, however, contact angle phenomena are complicated [9–11]. For example, the contact angle made by an advancing liquid (θ_a) and that made by a receding liquid (θ_r) are not identical. In general, nearly all solid surfaces exhibit contact angle hysteresis (the difference between θ_a and θ_r). Moreover, the experimentally observed apparent contact angle, θ , may or may not be equal to the Young contact angle, θ_Y [11]:

* Corresponding author. Tel: 001 416 978 1270;
Fax: 001 416 978 7753; e-mail: neumann@me.utoronto.ca

- (1) On ideal solid surfaces, there is no contact angle hysteresis and the experimentally observed contact angle is equal to θ_Y .
- (2) On smooth, but chemically heterogeneous solid surfaces, θ is not necessarily equal to the thermodynamic equilibrium angle. Nevertheless, the experimental advancing contact angle, θ_a , can be expected to be a good approximation of θ_Y . Therefore, care must be exercised to ensure that the experimental apparent contact angle, θ , is the advancing contact angle in order to be inserted into the Young equation.
- (3) On rough solid surfaces, no such equality between advancing contact angle and θ_Y exists. Thus, all contact angles on rough surfaces are meaningless in terms of Young's equation.

In addition to these complexities, penetration of the liquid into the solid, swelling of the solid by the liquid [12], and chemical reactions can all play a role. Experience has shown that polar surfaces often are non-inert because of their tendency to react with different liquids; non-polar surfaces, such as Teflon, and fluorocarbons FC-721 and FC-722, are often found to be quite inert and hence complexities such as chemical reaction may be minimized. In recent studies [13–15], it was shown that low-rate dynamic contact angles measured by an automated axisymmetric drop shape analysis-profile (ADSA-P) allows the determination of meaningful contact angles on non-inert copolymers, with no complications. Here, low-rate dynamic contact angles of 30 liquids on a fluorocarbon FC-725, a resin available from 3M (London, Ont.) that is chemically similar to the FC-721 and FC-722 used in other studies is reported [12,13,15–19]. Surprisingly, it turns out that FC-725 behaves differently from what one would expect for non-polar surfaces: slip/stick behaviour was observed with many liquids. This complicates the interpretation of contact angles in terms of Young's equation.

2. Materials (solid surfaces and liquids)

FC-725, a "Fluorad" brand conformal coating, available as a 2% solution from 3M, was used as

supplied. The FC-725-coated surfaces were prepared by a dip-coating technique [16] on cleaned and dried silicon wafer surfaces. Silicon wafers <100> (Silicon Sense, Naschua, NH; thickness: $525 \pm 50 \mu\text{m}$) were selected as the substrate for contact angle measurements. They were obtained as circular discs of ca 10 cm diameter and were cut into rectangular shapes of ca $2.5 \text{ cm} \times 5 \text{ cm}$. Each rectangular wafer surface was then soaked in chromic acid for at least 24 h, rinsed with doubly-distilled water, and dried under a heat lamp before dip-coating.

With respect to the low-rate dynamic contact angle measurements by ADSA-P, liquid was supplied to the sessile drop from below the wafer surfaces using a motorized syringe device [13]. In order to facilitate such an experimental procedure, a hole of ca 1 mm diameter was made, by using a diamond drill bit from Lunzer (New York, NY; SMS-0.027), in the centre of each rectangular wafer surface before soaking in chromic acid. In order to avoid leakage between a stainless steel needle (Chromatographic Specialities, Brockville, Ont; N723 needles pt. No. 3, H91023) and the hole (on the wafer surface), Teflon tape was wrapped around the end of the needle before inserting into the hole. In the literature, it is customary to first deposit a drop of liquid on a given solid surface using a syringe or a Teflon needle; the drop is then made to advance by supplying more liquid from above using a syringe or a needle in contact with the drop. Such experimental procedures cannot be used for ADSA-P since ADSA determines the contact angles and surface tensions based on the complete and undisturbed drop profile.

Thirty liquids were chosen in this study. Selection of these liquids was based on the following criteria:

- (1) liquids should include a wide range of intermolecular forces;
- (2) liquids should be non-toxic; and
- (3) the liquid surface tension should be higher than the anticipated solid surface tension [1,5,20].

They are listed in Table 1, together with the physical properties and surface tensions (measured at $23.0 \pm 0.5^\circ\text{C}$).

Table 1
Supplier, purity and surface tension of the liquids used

Liquid	Supplier	% Purity	Density (g cm ⁻³)	γ_{lv} (mJ m ⁻²)	No. of drops
Decane	Caledon	99.98	0.730	23.88 ± 0.008	10
Dodecane	Aldrich	99	0.749	25.64 ± 0.03	10
1-Pentanol	Aldrich	99+	0.811	26.01 ± 0.09	10
<i>trans</i> -Decalin	Aldrich	99	0.870	27.19 ± 0.08	10
Hexadecane	Aldrich	99+	0.773	27.62 ± 0.005	10
1-Decanol	Aldrich	99+	0.829	28.99 ± 0.004	10
<i>cis</i> -Decalin	Aldrich	99	0.897	32.32 ± 0.01	7
Nitromethane	Aldrich	99+	1.127	34.31 ± 0.006	10
2,5-Dichlorotoluene	Aldrich	98%	1.254	34.64 ± 0.003	10
Triacetin	Fluka	99+	1.158	35.52 ± 0.16	10
Ethyl cyanoacetate	Aldrich	98+	1.063	36.01 ± 0.04	9
<i>n,n</i> -Dimethylformamide	Sigma–Aldrich	99.9+(HPLC)	0.944	36.65 ± 0.004	10
Ethyl cinnamate	Aldrich	99	1.049	37.17 ± 0.02	10
Methyl salicylate	Aldrich	99+	1.174	38.82 ± 0.07	10
3,3-Thiodipropanol	Aldrich	98	1.092	39.83 ± 0.20	10
Dibenzylamine	Aldrich	97	1.026	40.80 ± 0.06	9
Dimethyl sulphoxide (DMSO)	Sigma–Aldrich	99.9 (HPLC)	1.101	42.68 ± 0.09	10
1-Iodonaphthalene	Aldrich	99	1.740	42.92 ± 0.03	10
1-Bromonaphthalene	Aldrich	98	1.489	44.31 ± 0.05	7
Diethylene glycol	Aldrich	99	1.118	45.16 ± 0.05	10
1,3-Diodopropane	Aldrich	99	2.576	46.51 ± 0.13	10
3-Pyridylcarbinol	Aldrich	98	1.124	47.81 ± 0.03	10
Ethanolamine	Aldrich	99+	1.012	48.23 ± 0.06	10
Ethylene glycol	Aldrich	99+	1.113	48.66 ± 0.06	10
1,1,2,2-Tetrabromoethane	Aldrich	98	2.967	49.29 ± 0.05	10
Diiodomethane	Aldrich	99	3.325	49.98 ± 0.02	10
2,2-Thiodiethanol	Aldrich	99+	1.221	53.77 ± 0.03	10
Formamide	Aldrich	99.5+	1.134	59.08 ± 0.04	10
Glycerol	Aldrich	99.5	1.261	63.13 ± 0.10	10
Water	LAST*	Doubly distilled	0.977	72.70 ± 0.09	10

*Laboratory of Applied Surface Thermodynamics.

3. Methods and procedures

ADSA-P is a technique to determine liquid–fluid interfacial tensions and contact angles from the shape of axisymmetric menisci, that is, from sessile as well as pendant drops. Assuming that the experimental drop is Laplacian and axisymmetric, ADSA-P finds a theoretical profile that best matches the drop profile extracted from an image of a real drop, from which the surface tension, contact angle, drop volume and surface area can be computed. Details of the methodology and experimental set-up can be found elsewhere [12,21–23].

Sessile drop experiments were performed by ADSA-P to determine contact angles. The temperature and relative humidity were maintained, respectively, at 23.0 ± 0.5°C and at ca 40%. It has been found that, since ADSA assumes an axisymmetric drop shape, the values of liquid surface tensions measured from sessile drops are very sensitive to even a very small amount of surface imperfection, such as roughness and heterogeneity, while contact angles are less sensitive. Therefore, the liquid surface tensions used in this study were independently measured by applying ADSA-P to a pendant drop, since the axisymmetry of the drop is enforced by using a circular capillary.

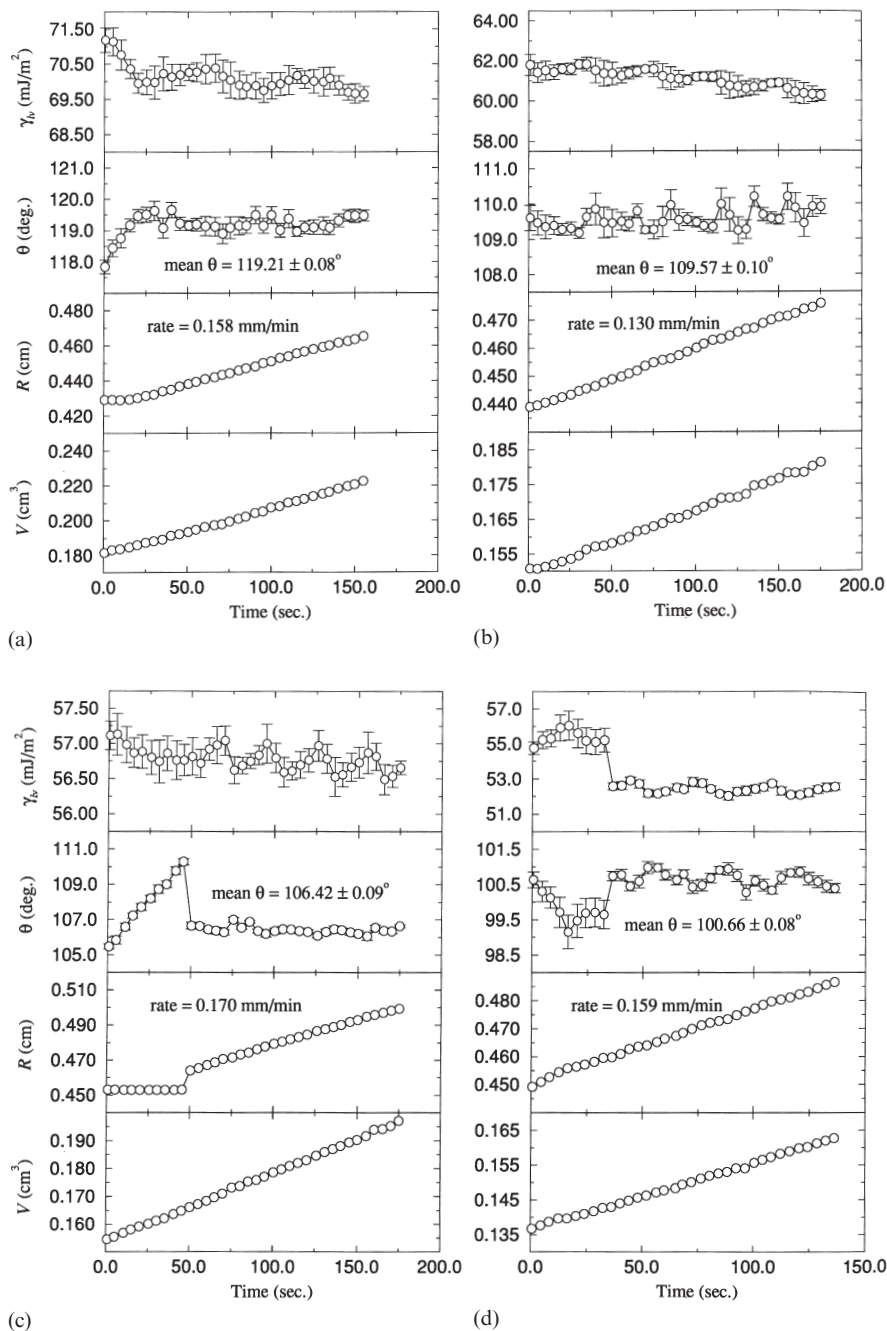


Fig. 1. Low-rate dynamic contact angles on a FC-725-coated silicon wafer surface for: (a) water; (b) glycerol; (c) formamide; (d) 2,2-thiodiethanol; (e) ethylene glycol; (f) diethylene glycol; (g) 3,3-thiodipropanol; (h) hexadecane; and (i) dodecane.

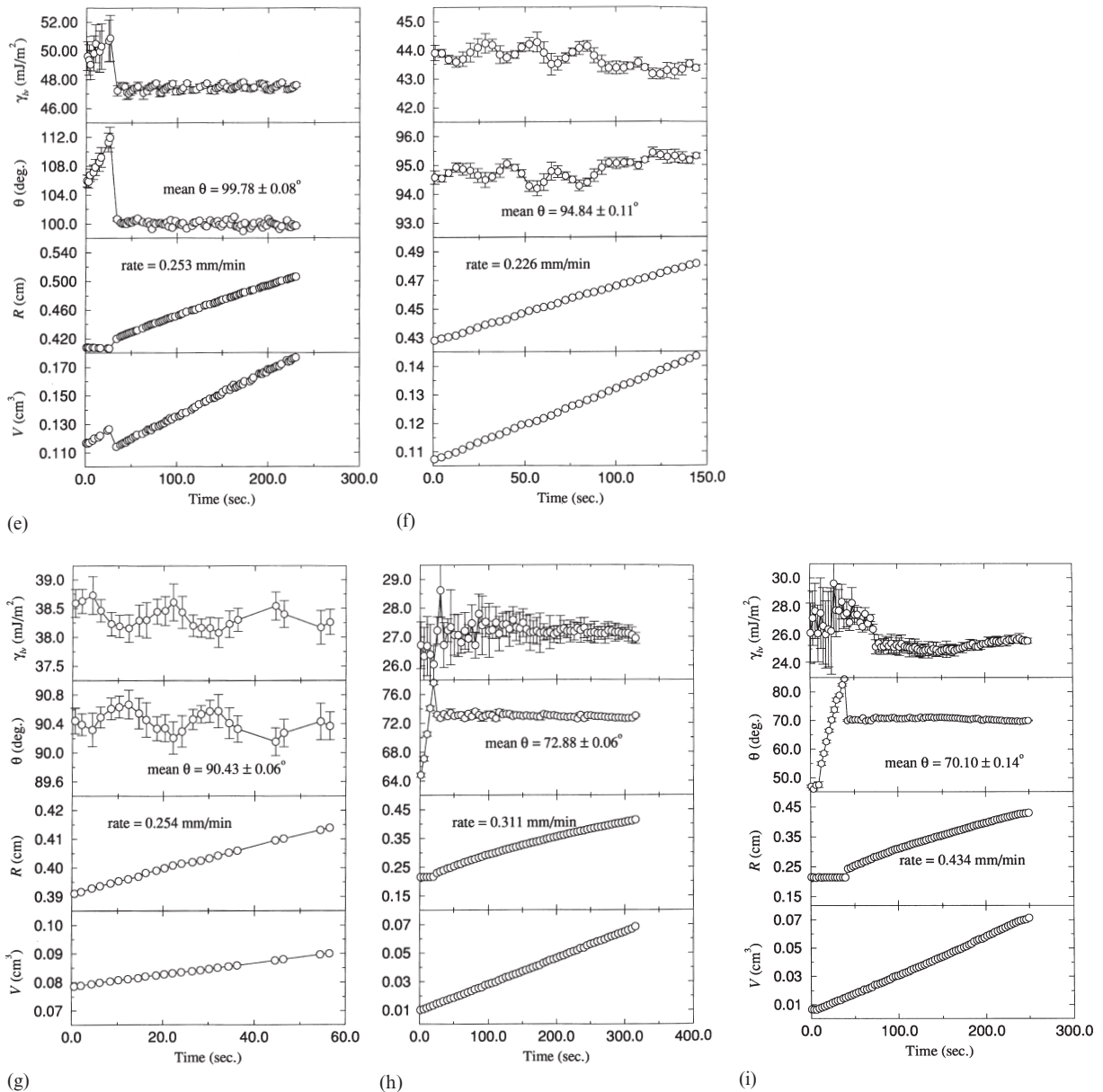


Fig. 1. (continued)

Results of the liquid surface tension are given in Table 1.

In this study, at least five and up to ten dynamic contact angle measurements (each on a newly prepared surface) at velocities of the three-phase contact line range from 0.1 to 0.8 mm min⁻¹ were performed for each liquid. The choice of this

velocity range was based on previous studies [13–15,18,24]: it has been shown that low-rate dynamic contact angles in this velocity range are essentially identical to the static contact angles, for these relatively smooth surfaces. Details of the experimental procedures have been described elsewhere [13–15].

4. Results and discussion

Of the 30 liquids used, only nine resulted in essentially constant contact angles: water; glycerol; formamide; 2,2-thiodiethanol; ethylene glycol; diethylene glycol; 3,3-thiodipropanol; hexadecane; and dodecane. Fig. 1(a) shows a typical experimental result of water: increasing the drop volume, V , linearly from 0.18 to ca 0.20 cm³ increases the apparent contact angle, θ , from ca 118 to 120° at essentially constant three-phase contact radius, R . This is due to the fact that even carefully putting an initial water drop from above on a solid surface can result in a contact angle somewhere between advancing and receding. This effect is more pronounced for liquids, such as water, which evaporate fast. Thus, further increase in the drop volume causes the three-phase contact line to advance, with θ essentially constant as R increases. Increasing the drop volume in this manner ensures the measured θ to be an advancing contact angle.

It should be noted that the liquid–vapour surface tensions calculated by ADSA-P sessile drop are fairly constant, but not as reliable as pendant drop, as explained above. The rate of advancing for this and similar experiments can be determined by linear regression from the linear region of the plot of the three-phase contact radius R over time: it was found that the drop periphery was being advanced at a rate of 0.16 mm min⁻¹, in this specific example. It turns out that averaging the measured contact angles after R reaches 0.45 cm is convenient, since the drop is guaranteed to be in the advancing mode and that line tension effects are negligible [19,25,26]; a mean contact angle of 119.21 ± 0.08° is obtained. The error limit in this case and the rest of the paper is the 95% confidence limit. While a three-phase contact radius of 0.45 cm may seem to be an arbitrary value, it turns out that there is virtually no dependence on the choice of the starting point. The reproducibility of this and other solid–liquid systems is excellent. They are summarized in Table 2 for the nine liquids with constant contact angles, at different rates of advancing and each on a newly prepared surface. A final θ value of 119.31 ± 0.22 was obtained for water. The 95% confidence limit calculated in this manner (in Table 2) includes all possible varia-

tions, for example, due to errors of the experiments, experimental technique and solid surface preparation.

The experimental results of other liquids with constant contact angles are shown in Fig. 1(b–i). The results, at different rates of advancing, are also included in Table 2. It can be seen in these figures that the three-phase line of formamide, ethylene glycol, hexadecane and dodecane appears to stick on the surface at the beginning of the experiment, but not once the drop has started advancing. This suggests that these liquids have a tendency to stick on the surface.

The rest of the 21 liquids were found to behave similarly on the surface, largely with slip/stick behaviour. Fig. 2(a) shows the contact angle results of diiodomethane. It can be seen that initially the apparent drop volume, as perceived by ADSA-P, increases linearly, and θ increases from 104 to 110° at essentially constant R . Suddenly, the drop front jumps to a new location as more liquid is supplied into the sessile drop. The resulting θ decreases sharply from 110 to 103°. As more liquid is supplied into the sessile drop, the contact angle increases again. Such slip/stick behaviour could be due to non-inertness of the surface. Phenomenologically, an energy barrier for the drop front exists, resulting in sticking, which causes θ to increase at constant R . However, as more liquid is supplied into the sessile drop, the drop front possesses enough energy to overcome the energy barrier, resulting in slipping, which causes θ to decrease suddenly. It should be noted that as the drop front jumps from one location to the next, it is unlikely that the drop will remain axisymmetric. Such a non-axisymmetric drop will obviously not meet the basic assumptions underlying ADSA-P, causing possible errors, for example, in the apparent surface tension and drop volume. This can be seen from the discontinuity of the apparent surface tension with time as the drop front sticks and slips. Obviously, the observed angles in Fig. 2(a) cannot all be the Young contact angles; since γ_{lv} , γ_{sv} (and γ_{sl}) are constants, θ ought to be a constant because of Young's equation. In addition, it is difficult to decide unambiguously at this moment whether or not Young's equation is applicable at all because of lack of understanding

Table 2

Summary of the dynamic (advancing) contact angles, θ ($^{\circ}$), at different rates (mm min^{-1}) of three-phase contact radius on a FC-725-coated wafer surface

Water		Glycerol		Formamide	
Rate	θ	Rate	θ	Rate	θ
0.084	119.20	0.102	111.54	0.104	106.93
0.095	119.13	0.105	111.08	0.121	107.67
0.099	119.35	0.114	109.96	0.129	107.13
0.136	119.38	0.117	109.94	0.141	106.26
0.142	118.93	0.118	109.74	0.162	107.16
0.158	119.21	0.127	109.89	0.163	106.64
0.168	119.48	0.128	109.77	0.170	106.42
0.207	119.76	0.129	109.97	0.195	106.89
—	—	0.130	109.97	—	—
—	—	—	—	—	—
Mean θ	119.31 ± 0.22		110.21 ± 0.49		106.89 ± 0.38
2,2-Thiodiethanol		Ethylene glycol		Diethylene glycol	
Rate	θ	Rate	θ	Rate	θ
0.159	100.66	0.181	100.05	0.121	94.04
0.163	101.02	0.182	100.04	0.192	94.90
0.164	101.19	0.183	100.38	0.202	94.16
0.181	100.70	0.207	99.98	0.221	93.89
0.184	100.76	0.253	99.78	0.226	94.84
0.239	100.71	0.266	99.91	0.246	94.78
0.250	101.35	0.297	100.07	0.260	94.69
0.321	101.18	0.441	100.01	—	—
0.354	101.58	0.536	100.13	—	—
0.644	101.53	0.548	100.18	—	—
Mean θ	101.07 ± 0.25		100.05 ± 0.12		94.47 ± 0.39
3,3-Thiodipropanol		Hexadecane		Dodecane	
Rate	θ	Rate	θ	Rate	θ
0.146	90.80	0.138	72.84	0.106	70.98
0.153	90.07	0.159	74.46	0.152	71.38
0.186	90.45	0.189	74.04	0.344	71.59
0.187	90.65	0.177	73.84	0.434	70.10
0.245	90.43	0.335	73.44	0.621	70.80
—	—	0.355	73.29	0.691	70.88
—	—	0.311	72.88	0.769	71.34
—	—	0.756	72.45	0.788	71.11
—	—	—	—	—	—
—	—	—	—	—	—
Mean θ	90.48 ± 0.34		73.41 ± 0.57		71.02 ± 0.39

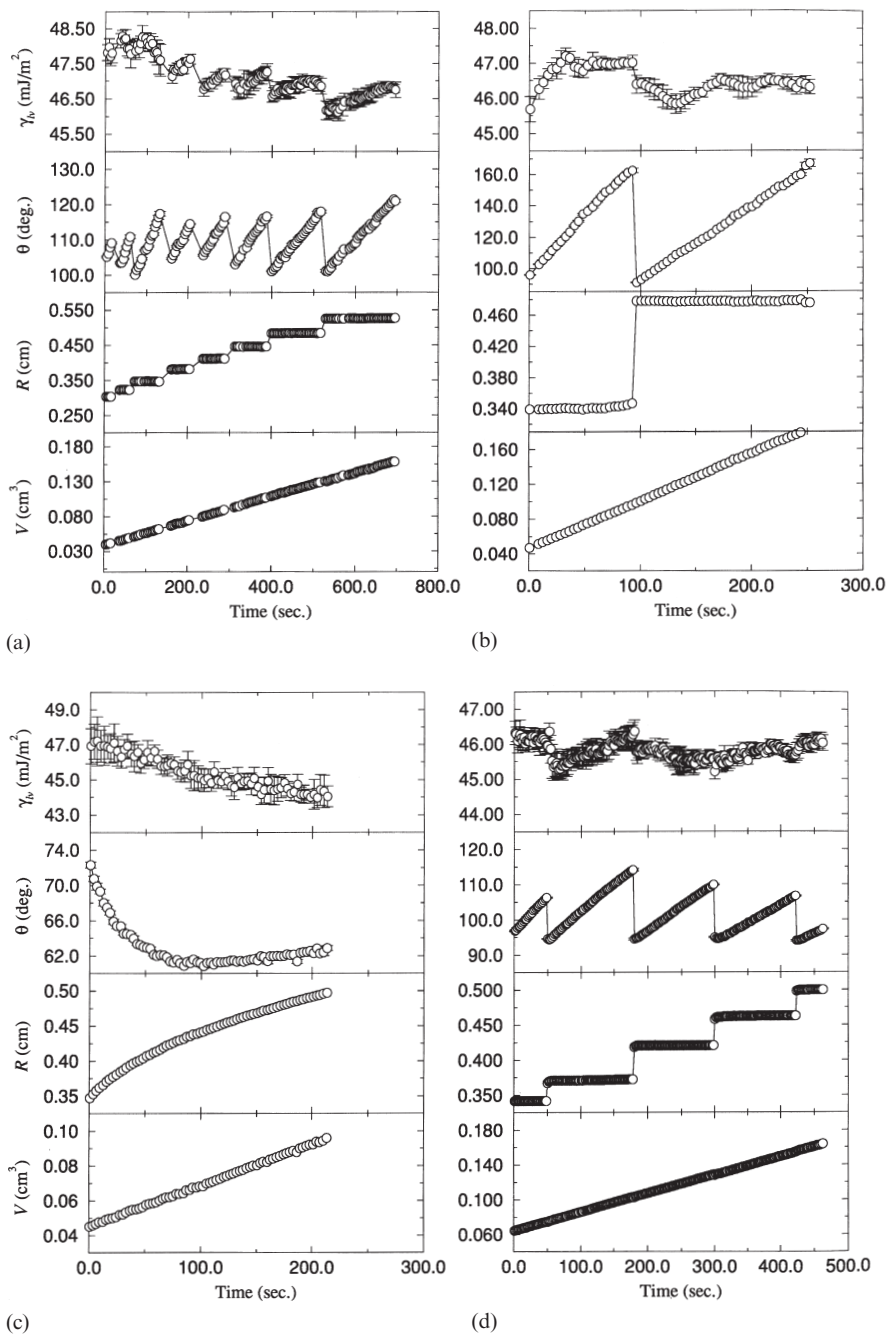


Fig. 2. Low-rate dynamic contact angles on a FC-725-coated wafer surface for: (a) diiodomethane; (b) 1,1,2,2-tetrabromoethane; (c) ethanolamine; (d) 3-pyridylcarbinol; (e) 1,3-diiodopropane; (f) 1-bromonaphthalene; (g) 1-iodonaphthalene; (h) dimethyl sulphoxide (DMSO); (i) dibenzylamine; (j) methyl salicylate; (k) ethyl cinnamate; (l) *n,n*-dimethylformamide; (m) ethyl cyanoacetate; (n) triacetin; (o) 2,5-dichlorotoluene; (p) nitromethane; (q) *cis*-decalin; (r) 1-decanol; (s) *trans*-decalin; (t) 1-pentanol; and (u) decane. These angles should not be used for the interpretation in terms of surface energetics, for reasons discussed in the text.

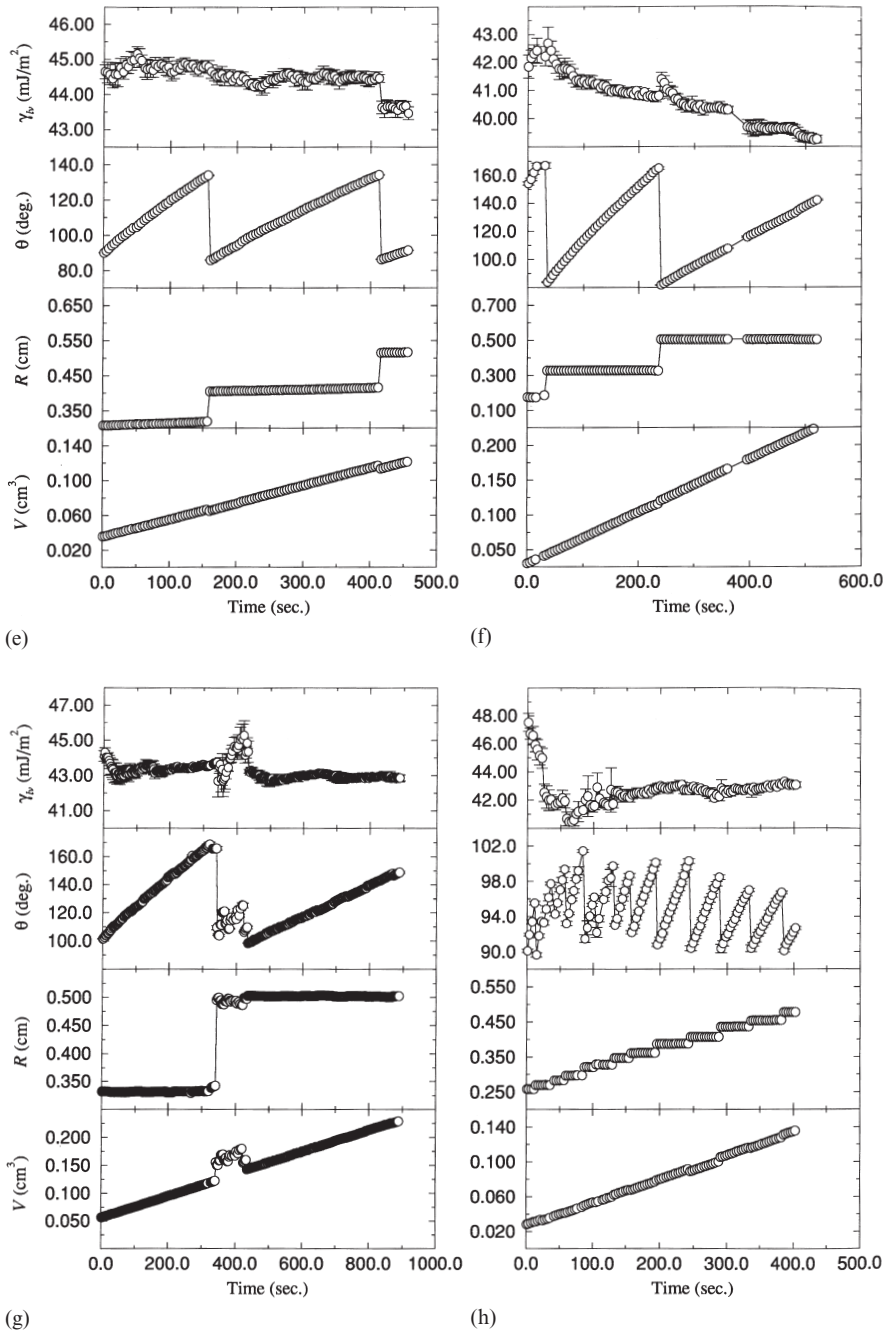


Fig. 2. (continued)

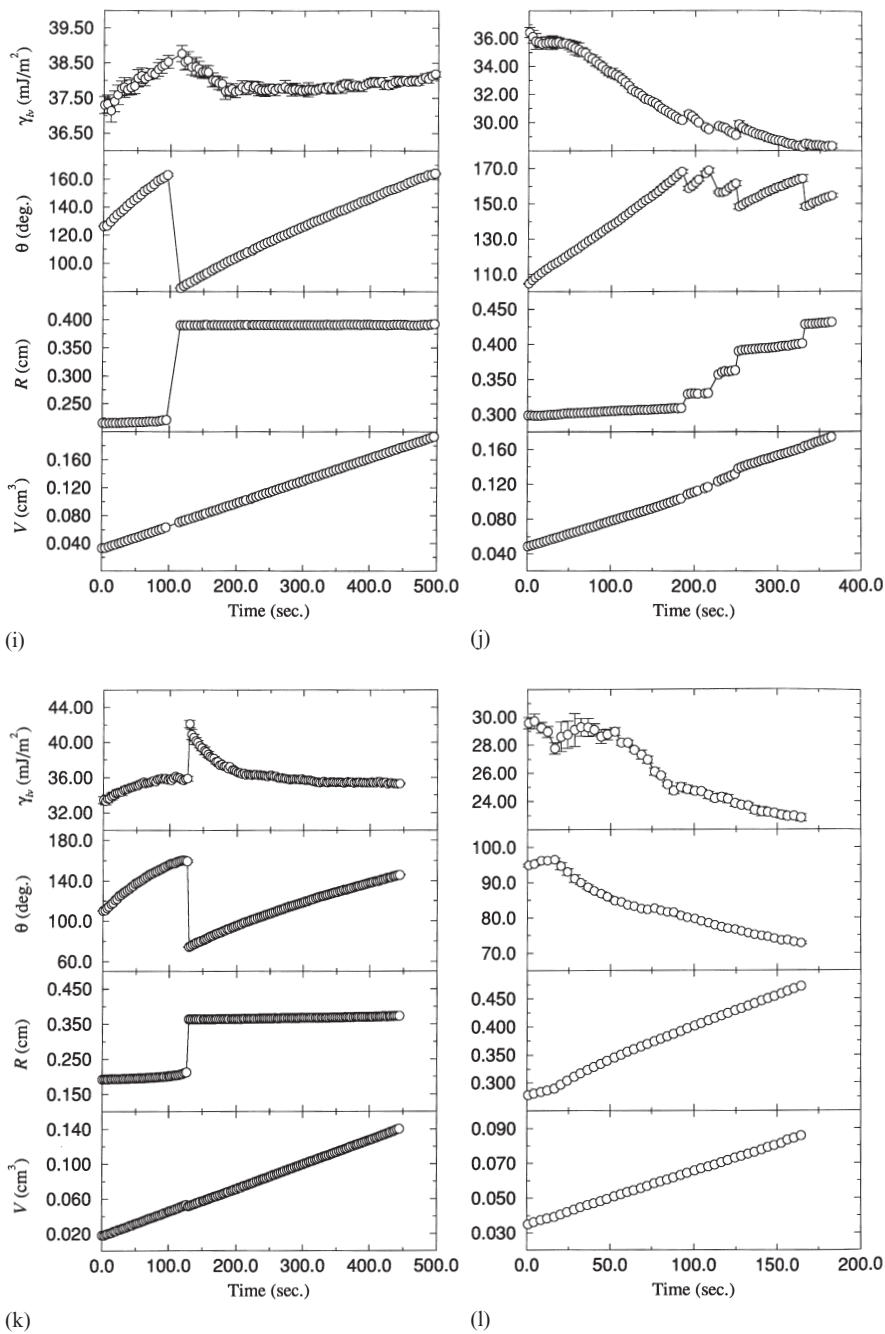


Fig. 2. (continued)

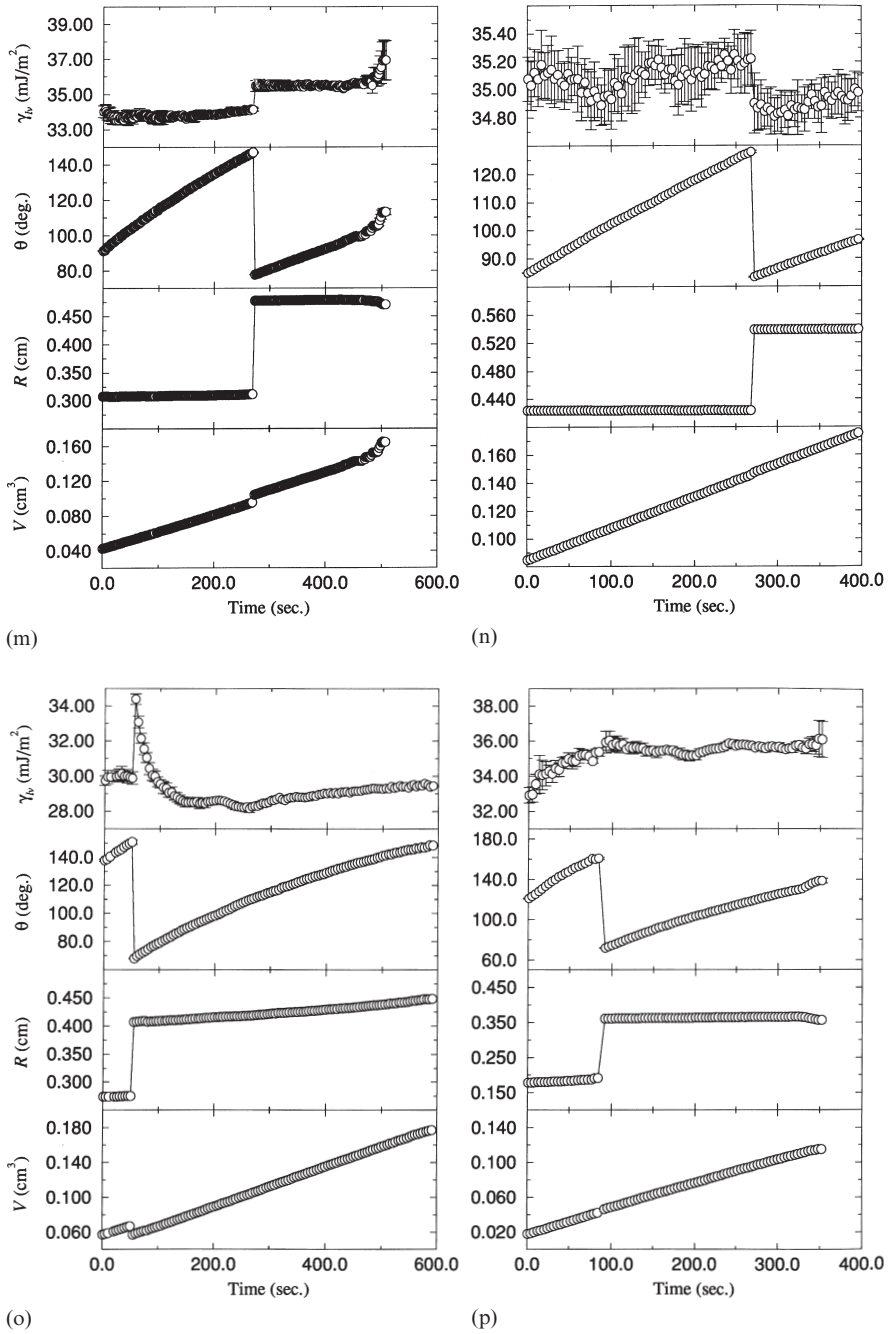


Fig. 2. (continued)

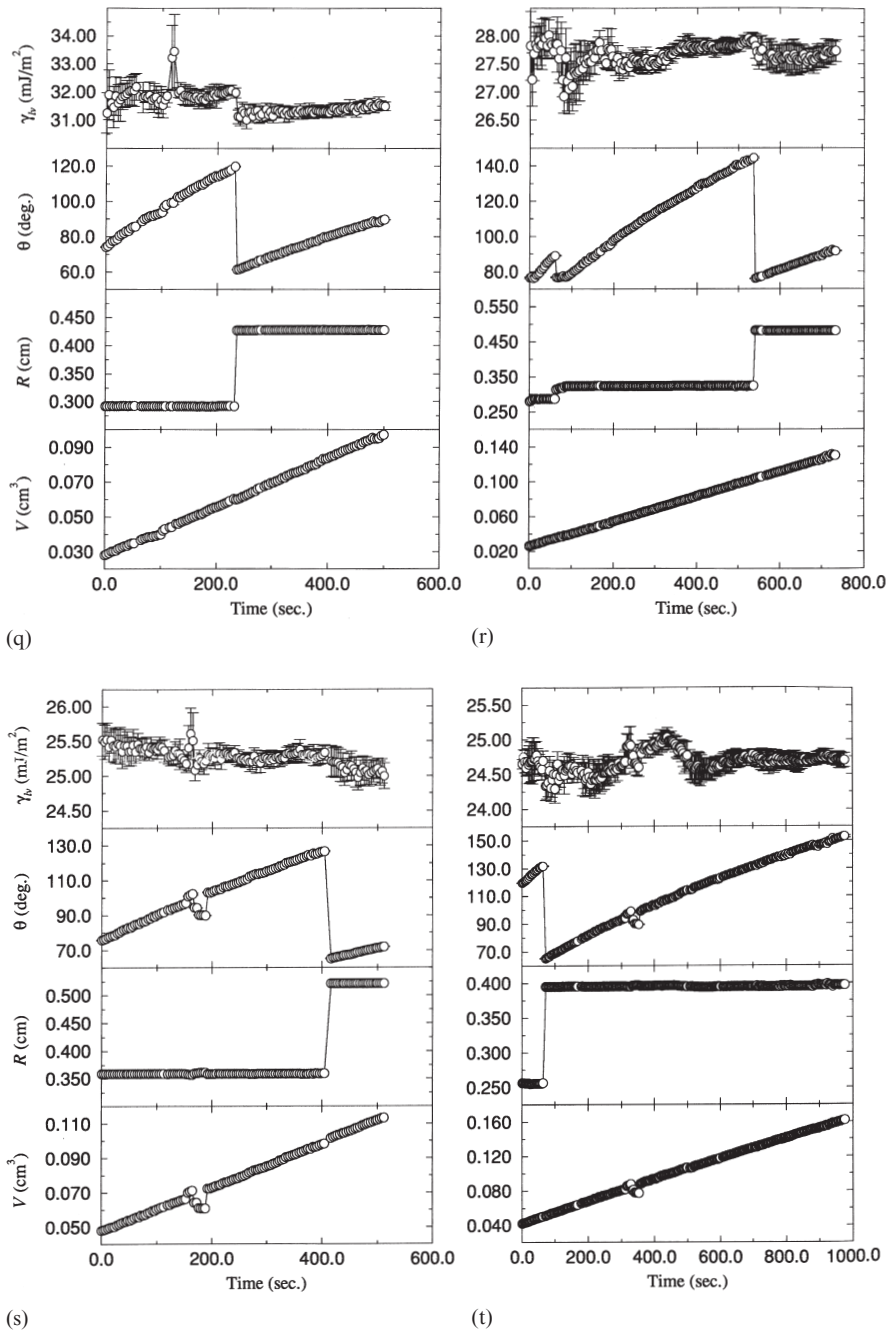
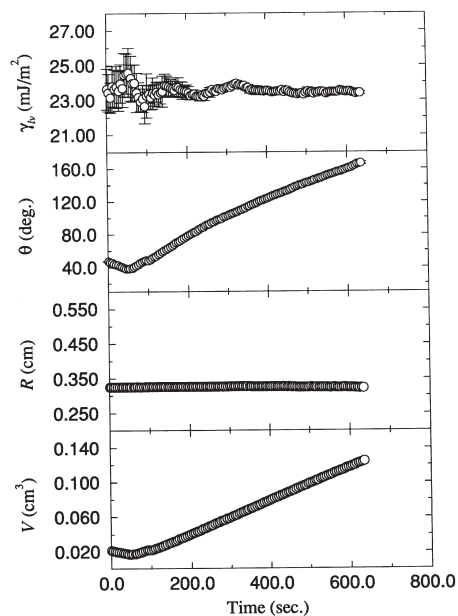


Fig. 2. (continued)



(u)

Fig. 2. (continued)

of the slip/stick mechanism. Therefore, these contact angles should not be used for the interpretation in terms of surface energetics. It should be mentioned that if one employs a conventional goniometer-sessile drop technique, a contact angle of ca 120° is likely to be obtained, that is, the maximum in the entire slip/stick pattern. This value is, of course, meaningless in terms of Young's equation, as explained above.

The experimental results of other liquids are either incompatible with Young's equation or possibly show physico-chemical reaction with the solid surface; they are shown in Fig. 2(b–u). It can be seen that many of the liquids yield slip/stick behaviour and, for reasons discussed above, these angles cannot be used for the interpretation in terms of surface energetics. In the worst case of such slip/stick mechanism, θ increases from ca 50 to 160° at essentially constant R . It should be noted that yet another contact angle pattern can be seen in Fig. 2(c and l), respectively, for ethanolamine and *n,n*-dimethylformamide. In both cases, γ_{lv} and θ decrease from that of the pure liquid and with time, suggesting that dissolution of the FC-725 by

the liquids occurs. Obviously, these angles should be disregarded for the following reasons:

- (1) γ_{lv} is different from that of the pure liquids;
- (2) it is unsure whether or not γ_{sl} and γ_{sv} remain constant and whether Young's equation is applicable.

A summary of these complexities is given in Table 3, together with the meaningful results from Table 2; a total of >150 freshly prepared FC-725-coated wafers were prepared and used; $>10\,000$ images were acquired and analysed by ADSA-P. The above observations cannot be made with a goniometer type of a technique: a goniometer cannot detect changes in γ_{lv} and hence the measurements are liable to produce a mixture of meaningful and meaningless contact angle data, with no criteria to distinguish between the two. This provides partial explanation of discrepancies of contact angles reported in the literature.

These experimental results should be confronted with a claim from van Oss et al. [27] that the study [28] of polar and non-polar liquids of the same surface tension yield the same contact angle is not conclusive:

If this demonstration were valid, it would work in the reverse sense, and liquids that have the same contact angle on a particular solid would be found to have the same surface tension. [27]

To support their claim, these authors reported contact angles of liquids of different surface tension, which nevertheless had the same contact angle on one and the same solid surface. The solid surfaces used were polymeric or biological in nature. Such observations were explained in terms of an additional effect of intermolecular forces (or surface tension components) on the contact angles. However, as can be seen in Fig. 2(a–u), it is not difficult for us to produce results of the type reported by the authors, simply by a goniometer technique (as van Oss et al. did) and/or poor surface quality. In the example given in Fig. 2(a) for diiodomethane, a contact angle of 120° is likely to be obtained if one employs a goniometer-sessile drop technique. This contact angle value is indeed nearly identical with that of the water, that is, 119.31° ; but the two liquids have very different surface tensions, just as observed [27]. However, in terms of Young's equation, the former angle is

Table 3

Low-rate dynamic (advancing) contact angles, θ ($^\circ$), measured by ADSA-P on a FC-725-coated wafer surface

Liquid	γ_{lv} (mJ m $^{-2}$)	θ
Decane	23.88	Slip/stick (50 $^\circ$ →160 $^\circ$)
Dodecane	25.64	71.02 ± 0.39
1-Pentanol	26.01	Slip/stick (65 $^\circ$ →150 $^\circ$)
<i>trans</i> -Decalin	27.19	Slip/stick (75 $^\circ$ →130 $^\circ$)
Hexadecane	27.62	73.41 ± 0.57
1-Decanol	28.99	Slip/stick (80 $^\circ$ →140 $^\circ$)
<i>cis</i> -Decalin	32.32	Slip/stick (70 $^\circ$ →120 $^\circ$)
Nitromethane	34.31	Slip/stick (70 $^\circ$ →140 $^\circ$)
2,5-Dichlorotoluene	34.64	Slip/stick (70 $^\circ$ →150 $^\circ$)
Triacetin	35.53	Slip/stick (85 $^\circ$ →130 $^\circ$)
Ethyl cyanoacetate	36.01	Slip/stick (90 $^\circ$ →150 $^\circ$)
<i>n,n</i> -Dimethylformamide	36.65	θ ↓ and γ_{lv} ↓ as R ↑ (95 $^\circ$ →70 $^\circ$)
Ethyl cinnamate	37.17	Slip/stick (70 $^\circ$ →140 $^\circ$)
Methyl salicylate	38.82	Slip/stick (105 $^\circ$ →165 $^\circ$)
3,3-Thiodipropanol	39.83	90.48 ± 0.34
Dibenzylamine	40.80	Slip/stick (80 $^\circ$ →160 $^\circ$)
Dimethyl sulphoxide (DMSO)	42.68	Slip/stick (90 $^\circ$ →100 $^\circ$)
1-Iodonaphthalene	42.92	Slip/stick (100 $^\circ$ →170 $^\circ$)
1-Bromonaphthalene	44.31	Slip/stick (80 $^\circ$ →160 $^\circ$)
Diethylene glycol	45.16	94.47 ± 0.39
1,3-Diiodopropane	46.51	Slip/stick (95 $^\circ$ →135 $^\circ$)
3-Pyridylcarbinol	47.81	Slip/stick (95 $^\circ$ →115 $^\circ$)
Ethanolamine	48.23	θ ↓ and γ_{lv} ↓ as R ↑ (73 $^\circ$ →60 $^\circ$)
Ethylene glycol	48.66	100.05 ± 0.12
1,1,2,2-Tetrabromoethane	49.29	Slip/stick (95 $^\circ$ →160 $^\circ$)
Diiodomethane	49.98	Slip/stick (98 $^\circ$ →123 $^\circ$)
2,2-Thiodiethanol	53.77	101.07 ± 0.25
Formamide	59.08	106.89 ± 0.38
Glycerol	63.13	110.21 ± 0.49
Water	72.70	119.31 ± 0.22

meaningless; the latter one is meaningful. Thus, the above claim of these authors is misleading.

Disregarding the inconclusive contact angle data in Fig. 2, Fig. 3 shows the contact angle results of Table 2, by plotting $\gamma_{lv} \cos \theta$ versus γ_{lv} . It can be seen that liquids with very different molecular structure fall on a smooth curve, in good agreement with the results from previous studies [13–17,29]. It is concluded, once again, that $\gamma_{lv} \cos \theta$ depends only on γ_{lv} for a given solid surface (constant γ_{sv}) and not explicitly on the intermolecular forces:

$$\gamma_{lv} \cos \theta = f(\gamma_{lv}, \gamma_{sv}) \quad (2)$$

Because of Young's equation, Eq. (2) can be rewritten as

$$\gamma_{sl} = F(\gamma_{lv}, \gamma_{sv}) \quad (3)$$

While the experimental results clash directly with the surface tension component approaches [2,6–8], they allow one search for a relation in the form of Eq. (3). However, if any of the inconclusive data (due to inadequate experimentation and/or non-inertness of the surface) in Fig. 2 were included in Fig. 3, scatter would result and hence a rather different conclusion would be drawn: one would then argue that $\gamma_{lv} \cos \theta$ for a given solid surface depends not only on γ_{lv} , but also on the effect of intermolecular forces (or surface tension components) on the contact angles.

On phenomenological grounds, an equation-of-state approach for solid–liquid interfacial tension has been formulated [5]:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}}e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \quad (4)$$

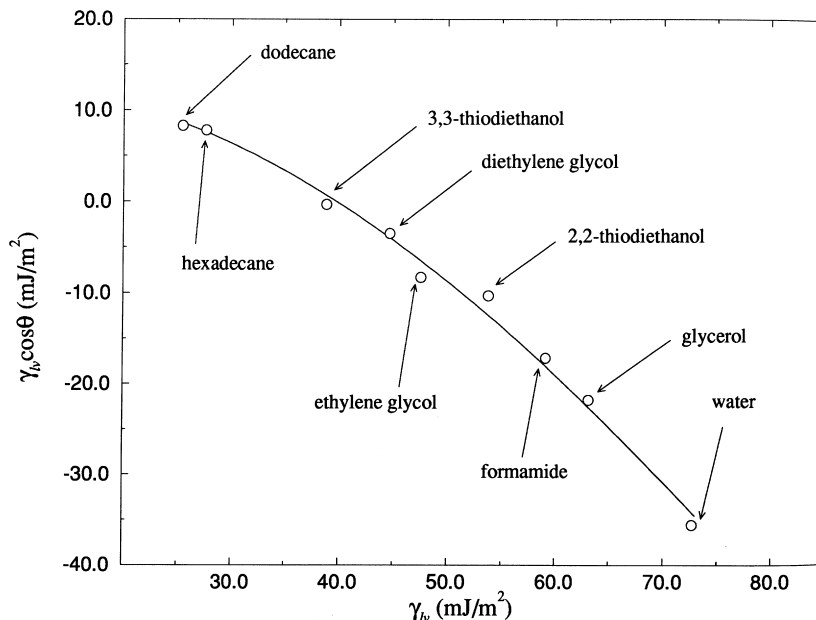


Fig. 3. The values of $\gamma_{lv} \cos \theta$ versus γ_{lv} for the FC-725 surface, for the data in Table 2. Since the values of $\gamma_{lv} \cos \theta$ change smoothly with γ_{lv} at constant γ_{sv} , intermolecular forces (or surface tension components) do not have any independent effects on the contact angles. Because of Young's equation, γ_{sl} can be expressed as a function of only γ_{lv} and γ_{sv} .

where β is a constant which was found to be $0.0001247 \text{ (m}^2 \text{ mJ}^{-1})^2$. Combining this equation with Young's equation yields.

$$\cos \theta_Y = -1 + 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \quad (5)$$

Thus, the solid surface tensions can be determined from experimental (Young) contact angles and liquid surface tensions.

The applicability of any approach having the form of Eq. (3) can be tested using the criteria of the constancy of the calculated γ_{sv} values. It is shown in Table 4 the γ_{sv} values calculated from Antonow's rule [30], Berthelot's rule [31] and the equation-of-state approach for solid–liquid interfacial tensions [5], which can be understood as a modified Berthelot's rule [32]. It can be seen that the values of γ_{sv} calculated from Antonow's rule increase as γ_{lv} increases; the γ_{sv} values calculated from Berthelot's rule decrease as γ_{lv} increases. Only the γ_{sv} values from the equation-of-state approach for solid–liquid interfacial tensions are quite constant, essentially independent of the liquids used:

the γ_{sv} value of FC-725-coated silicon wafer was found to be 12.28 mJ m^{-2} with a 95% confidence limit of $\pm 0.42 \text{ mJ m}^{-2}$.

It should be noted that the constant β value of $0.0001247 \text{ (m}^2 \text{ mJ}^{-1})^2$ used in the above calculations was determined only from the contact angle data on three well-prepared solid surfaces [16]: FC-721-coated mica, heat-pressed Teflon (FEP), and poly(ethylene terephthalate) (PET). Alternatively, the γ_{sv} value of FC-725 can be determined by a two-variable least-square analysis [5], by assuming γ_{sv} and β in Eq. (5) to be constant. Employing the set of contact angle data on FC-725, a β value of $0.0001188 \text{ (m}^2 \text{ mJ}^{-1})^2$ and a γ_{sv} value of 12.11 mJ m^{-2} are obtained. It is evident that there is good agreement between the γ_{sv} values (12.28 ± 0.42 and 12.11 mJ m^{-2}) determined from the two procedures. However, it might be argued that the two β values are different. To show that such a difference is of little consequence with respect to the determination of γ_{sv} , the γ_{sv} values of a hypothetical system having $\gamma_{lv} = 50 \text{ mJ m}^{-2}$ and $\theta = 50^\circ$ for the above β values are determined.

Table 4

Solid–vapour surface tensions, γ_{sv} (mJ m^{-2}), of FC-725-coated wafer calculated from Antonow's rule, Berthelot's rule, and an equation-of-state approach for solid–liquid interfacial tensions

Liquid	γ_{lv} (mJ m^{-2})	θ ($^\circ$)	γ_{sv}		
			Antonow's rule [30]	Berthelot's rule [31]	Equation-of-state approach [5]
Dodecane	25.64	71.02	16.99	11.26	11.81
Hexadecane	27.62	73.41	17.75	11.41	12.12
3,3-Thiodipropanol	39.83	90.48	19.75	9.79	11.90
Diethylene glycol	45.16	94.47	20.82	9.60	12.53
Ethylene glycol	48.66	100.05	20.08	8.29	11.58
2,2-Thiodiethanol	53.77	101.07	21.72	8.78	13.22
Formamide	59.08	106.89	20.96	7.43	12.71
Glycerol	63.13	110.21	20.66	6.76	12.74
Water	72.70	119.31	18.56	4.74	11.91

It turns out that there are virtually no differences in the calculated γ_{sv} values: $\gamma_{sv} = 35.54 \text{ mJ m}^{-2}$ when $\beta = 0.0001247 \text{ (m}^2 \text{ mJ}^{-1})^2$ and $\gamma_{sv} = 35.47 \text{ mJ m}^{-2}$ when $\beta = 0.0001182 \text{ (m}^2 \text{ mJ}^{-1})^2$. The above results indeed reconfirm the validity of the equation-of-state approach to determine solid surface tensions from contact angles.

5. Conclusions

- (1) Interpreting experimental contact angles for surface energetics is difficult: meaningful contact angle experiments require considerable experimental care and suitable methodology; the conventional goniometer technique does not qualify.
- (2) The claim of van Oss et al. [27] that liquids with the same contact angles do not have the same surface tensions is misleading.
- (3) Circumspection is necessary in the decision whether or not experimental contact angles can be used in conjunction with Young's equation and whether or not the contact angles violate the assumptions made in all contact angle approaches, as stated before [14,15].
- (4) If one omits the inconclusive contact angle measurements, the values of $\gamma_{lv} \cos \theta$ change smoothly with γ_{lv} for FC-725, in excellent agreement with other polar and non-polar surfaces from other studies [13,17,29].

- (5) While intermolecular forces determine the interfacial tensions, they do not have additional effects on the contact angles: hence the surface tension component approaches [2,6–8] cannot describe physical reality.
- (6) The γ_{sv} values of FC-725 calculated from the equation-of-state approach [5] are essentially constant, independent of the liquids used. This reconfirms the soundness of the approach to calculate solid surface tensions from contact angles.

Acknowledgment

This paper represents, in part, the Ph.D. thesis of D.Y. Kwok. This research was supported by the Natural Science and Engineering Research Council of Canada (Grants Nos A8278 and EQP173469), Ontario Graduate Scholarships (D.Y.K.) and University of Toronto Open Fellowships (D.Y.K.).

References

- [1] W.A. Zisman, Contact angle, wettability and adhesion, in: *Advances in Chemistry Series*, Vol. 43, American Chemical Society, Washington, DC, 1964.
- [2] F.M. Fowkes, *Ind. Eng. Chem.* 12 (1964) 40.
- [3] O. Driedger, A.W. Neumann, P.J. Sell, *Kolloid-Z. Z. Polym.* 201 (1965) 52.

- [4] A.W. Neumann, R.J. Good, C.J. Hope, M. Sejpal, *J. Colloid Interface Sci.* 49 (1974) 291.
- [5] J.K. Spelt, D. Li, The equation of state approach to interfacial tensions, in: A.W. Neumann, J.K. Spelt (Eds.), *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996, pp. 239–292.
- [6] D.K. Owens, R.C. Wendt, *J. Appl. Polym. Sci.* 13 (1969) 1741.
- [7] C.J. van Oss, M.K. Chaudhury, R.J. Good, *Chem. Rev.* 88 (1988) 927.
- [8] R.J. Good, C.J. van Oss, The modern theory of contact angles and the hydrogen bond components of surface energies, in: M. Schrader, G. Loeb. (Eds.), *Modern Approaches to Wettability: Theory and Applications*, Plenum Press, New York, 1992, pp. 1–27.
- [9] A.W. Neumann, *Adv. Colloid Interface Sci.* 4 (1974) 105.
- [10] A. Marmur, *Colloids Surf. A* 116 (1996) 25.
- [11] D. Li, A.W. Neumann, Thermodynamic status of contact angles, in: A.W. Neumann, J.K. Spelt (Eds.) *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996, pp. 109–168.
- [12] R.V. Sedev, J.G. Petrov, A.W. Neumann, *J. Colloid Interface Sci.* 180 (1996) 36.
- [13] D.Y. Kwok, R. Lin, M. Mui, A.W. Neumann, *Colloids Surf. A* 116 (1996) 63.
- [14] D.Y. Kwok, T. Gietzelt, K. Grundke, H.-J. Jacobasch, A.W. Neumann, *Langmuir* 13 (1997) 2880.
- [15] O.I. del Río, D.Y. Kwok, R. Wu, J.M. Alvarez, A.W. Neumann, Contact angle measurements by axisymmetric drop shape analysis and an automated polynomial fit program. *Colloid Surf. A* accepted.
- [16] D. Li, A.W. Neumann, *J. Colloid Interface Sci.* 148 (1992) 190.
- [17] D. Li, M. Xie, A.W. Neumann, *Colloid Polym. Sci.* 271 (1993) 573.
- [18] D.Y. Kwok, C.J. Budziak, A.W. Neumann, *J. Colloid Interface Sci.* 173 (1995) 143.
- [19] D. Duncan, D. Li, J. Gaydos, A.W. Neumann, *J. Colloid Interface Sci.* 169 (1995) 256.
- [20] K. Grundke, T. Bogumil, T. Gietzelt, H.-J. Jacobasch, D.Y. Kwok, A.W. Neumann, *Prog. Colloid Polym. Sci.* 101 (1996) 58.
- [21] Y. Rotenberg, L. Boruvka, A.W. Neumann, *J. Colloid Interface Sci.* 93 (1983) 169.
- [22] P. Cheng, D. Li, L. Boruvka, Y. Rotenberg, A.W. Neumann, *Colloids Surf.* 93 (1983) 169.
- [23] S. Lahooti, O.I. del Roío, P. Cheng, A.W. Neumann, Axisymmetric drop shape analysis, in: A.W. Neumann, J.K. Spelt, (Eds.), *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996, pp. 441–507.
- [24] D.Y. Kwok, D. Li, A.W. Neumann, Capillary rise at a vertical plate as a contact angle technique, in: A.W. Neumann, J.K. Spelt (Eds.), *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996, pp. 413–440.
- [25] D. Li, A.W. Neumann, *Adv. Colloid Interface Sci.* 39 (1992) 347.
- [26] J. Gaydos, A.W. Neumann, Line tension in multiphase equilibrium systems, in: A.W. Neumann, J.K. Spelt (Eds.), *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996, pp 169–238.
- [27] C.J. van Oss, R.J. Good, M.K. Chaudhury, *Langmuir* 4 (1988) 884.
- [28] J.K. Spelt, D.R. Absolom, A.W. Neumann, *Langmuir* 2 (1986) 620.
- [29] D.Y. Kwok, D. Li, A.W. Neumann, *Colloids Surf. A* 89 (1994) 181.
- [30] G. Antonow, *J. Chim. Phys.* 5 (1907) 372.
- [31] D. Berthelot, *Compt. rend.* 126 (1898) 1703 1857
- [32] D. Li, A.W. Neumann, *J. Colloid Interface Sci.* 137 (1990) 304.