

Interaction Forces Involved in Wetting of Human Skin

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Abstract □ Wetting of human skin by several liquids was investigated by contact angle measurements. Excised and live skin exhibited similar wetting properties. The skin surface was found to be hydrophobic, with little or no polar interaction occurring between the wetting liquid and the skin surface. The Good-Girafalco-Fowkes-Young equation can be used to predict contact angles of liquids on human skin.

Keyphrases □ Wettability of human skin—hydrophobic interactions, determination of critical surface tension, contact angles predicted □ Skin (human) wettability—hydrophobic interactions, determination of critical surface tension, contact angles predicted □ Surface tension, critical—determination for human skin, used to predict contact angles □ Contact angles of liquids on excised and live human skin—predicted from critical surface tension determinations, used to study wettability

The subject of wetting has been a major concern of surface scientists from both an applied and a fundamental approach. Important industrial applications such as transfer of ink in printing, dirt removal, flotation, and disintegration of tablets all involve wetting phenomena. Fundamental investigations of wetting are concerned with surface energies of solids, surface roughness, forces involved in the wetting process, and thermodynamic considerations. Several reviews of various aspects of wetting are available in the literature (1-5).

Wettability is normally described in terms of contact angles (θ) (*i.e.*, the internal angle between the solid surface and a liquid droplet applied to that surface). High contact angles mean poor wetting while low angles signify good wetting. If a liquid spreads on the solid surface, the contact angle is considered zero and complete wetting is said to occur.

Relatively few studies of wetting of human skin have been reported. Adamson *et al.* (7) and Ginn *et al.* (8) reported that water contact angles on clean degreased human skin usually exceed 100° . Additionally, Ginn *et al.* determined the critical surface tension of skin to be 26.8 dynes/cm. using an acetone-water series. More recently, Schott (9) reported contact angles of water on human skin which are somewhat lower compared to those reported previously.

The above work clearly shows that human skin is a hydrophobic surface. The wetting of any surface can be considered as related to a combination of two types of forces operative between the liquid and the surface: polar and nonpolar (10, 11). The relative contribution of each of these forces in human skin has not previously been determined. By measuring contact angles of several liquids of varying polarity and employing the Good-Girafalco-Fowkes-Young equation (GGFY) (10-13), we intend to establish the dominant type of interaction occurring between skin and the wetting liquid, determine the critical surface tension of skin, and predict contact angle values from a knowledge of the critical

Table I—Contact Angles (θ) Obtained on Live and Excised Human Skin^a

Compound	θ Live, degrees	θ Excised, degrees
Water	108 ± 4.1	107 ± 2.0
Glycerol	86 ± 3.1	91 ± 4.3
Formamide	79 ± 6.9	85 ± 5.4
Diiodomethane	55 ± 6.9	54 ± 6.3
Tetrabromoethane	42 ± 4.6	39 ± 4.9
Ethylene glycol	70 ± 4.5	69 ± 3.6
Benzyl alcohol	41 ± 5.1	32 ± 2.6
Tetrachloroethane	0	0
Mineral oil	0	0
Decahydronaphthalene	0	0

^a Results are quoted ± SD of the parameter.

surface tension of skin and the polar and dispersion components of surface tension of the wetting liquid. We also report that there is no significant difference between wetting properties of excised and live human skin.

EXPERIMENTAL

Contact angles were measured with a contact angle goniometer¹ equipped with a specially designed finger holder. For live subjects the dorsal areas of the ring and forefingers were used. Female breast skin was employed for excised skin investigations. The excised skin was kept frozen before use.

All measurements were made by the sessile drop method using advancing angles at 25° . For each contact angle determination, the average value of three droplets, reading both sides of the drop, was designated as the contact angle. Generally, 2-10- μ l. droplets were employed. Ten subjects were used for live studies, while six pieces of excised skin were employed. Angles obtained in this manner were reproducible to within $\pm 2^\circ$ for each individual liquid on a specific subject or piece of excised skin.

To obtain contact angles on clean degreased skin, the skin was thoroughly washed with soap and water, rinsed several times with absolute ethanol, rinsed with distilled water, and finally hot air dried. Contact angles of water on skin cleaned in this manner were always greater than 100° .

The purity of the liquids was checked by GC. Surface tensions were measured with a tensiometer² using appropriate ring correction factors.

Paraffin³ [specified as wax, refined, m.p. $56.1-57.1^\circ$ ($133-135^\circ\text{F.}$)] was used for contact angle determinations. Smooth paraffin surfaces were obtained by melting the wax on glass slides.

RESULTS AND DISCUSSION

In Vivo-In Vitro Comparison—Table I shows a comparison of contact angles of several liquids on clean excised skin with those measured using live skin. Good agreement was obtained, demonstrating that excised skin can be used as a model for studying the wetting properties of living human skin. The use of excised skin can simplify wetting studies since the problem of obtaining and controlling live panels is avoided. Additionally, toxic liquids can be used if excised skin is employed.

¹ Ramé-Hart.

² Cenco-Du-Nuoy.

³ Mobil Oil Corp.

Table II—Dispersion and Polar Components of Total Surface Tension of Acetone–Water Mixtures Calculated from Contact Angles on Paraffin

Weight Percent Acetone	Contact Angle (θ), degrees	cos θ	Total Surface Tension (γ _L), dynes/cm.	Dispersion Component (γ _{LD}), dynes/cm.	Polar Component (γ _{LP}), dynes/cm.
0.00	108	-0.309	71.3	23.8	47.5
4.77	95	-0.087	56.5	26.1	30.4
9.67	90	0.000	49.6	24.1	25.5
14.58	85	0.087	44.4	22.9	21.5
19.87	77	0.225	41.4	25.2	16.2
36.60	65	0.423	34.2	23.2	11.0
45.97	59	0.515	31.7	22.6	9.1
50.00	53	0.602	30.4	23.3	7.1
60.20	53	0.602	28.9	21.0	7.9

Wetting of Skin—As described by Dann (10, 11), the GGFY equation relates contact angles to various physicochemical parameters as follows:

$$\cos \theta = (-\gamma_L + 2\sqrt{\gamma_S D \gamma_{LD}} - \pi_S) / (\gamma_L - \pi_L) \quad (\text{Eq. 1})$$

Here θ is the contact angle, γ_L is the surface tension of the liquid, $\gamma_S D$ is the dispersion force component of the solid, γ_{LD} is the dispersion force component of the liquid, π_S is the reduction in surface energy of the solid resulting from adsorption of vapor from liquid L , and π_L is the reduction in surface energy of the liquid resulting from adsorption of a film of solid material from the solid. As a first approximation, π_S and π_L are assumed to be negligible for low energy solids (10) and are neglected in the calculation.

Dann (10, 11) showed that the determination of critical surface tensions, as obtained by the Zisman method (6), can be misleading as it does not account for the specific type of interaction force involved in the wetting process as used in Eq. 1.

Figure 1 is a Zisman plot (6) for measurements made using an acetone–water series. The critical surface tension for excised skin (γ_C) is determined to be 27.5 dynes/cm., in good agreement with that previously published (8). From contact angle measurements of the acetone–water series on paraffin, the contribution of dispersion and polar forces to the surface tension of each mixture was determined from the following equation:

$$\sqrt{\gamma_{LD}} = (\cos \theta + 1) \gamma_L / 2\sqrt{\gamma_S D} \quad (\text{Eq. 2})$$

which is a rearranged version of Eq. 1, assuming $\pi_L = \pi_S = 0$

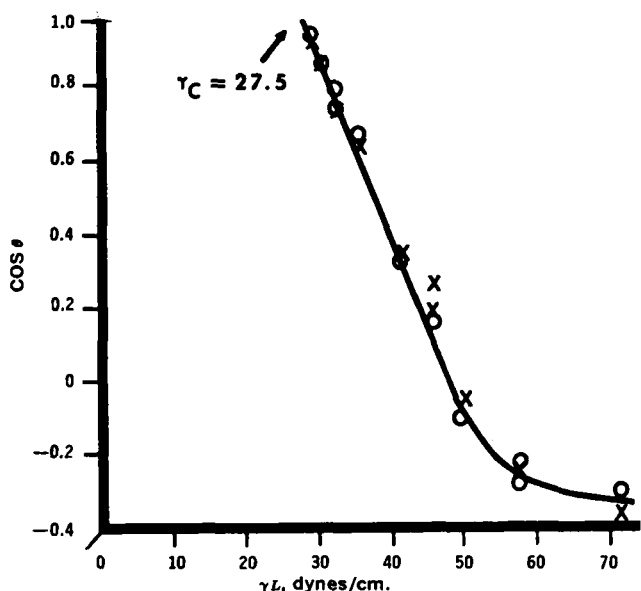


Figure 1—Zisman plot for wetting of excised human skin by acetone–water mixtures. Extrapolating the curve to $\cos \theta = 1.0$ results in $\gamma_C = 27.5$ dynes/cm.

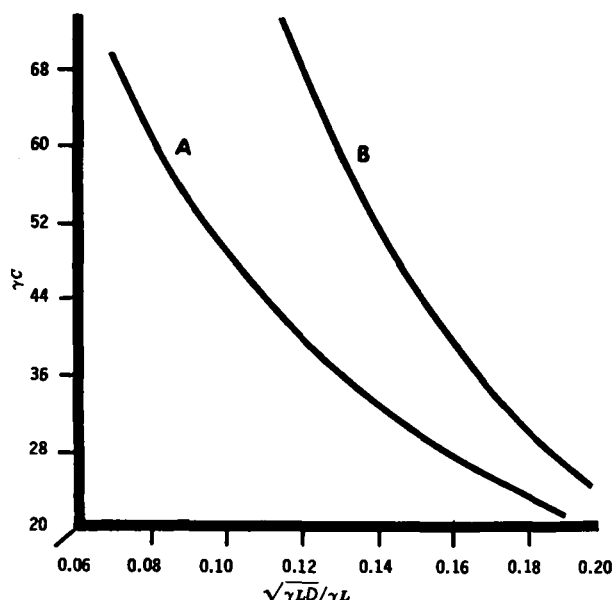


Figure 2—Critical surface tension conversion plot according to the method of Dann (10). Curve A is obtained using the data in Table II for the acetone–water series. Curve B is constructed assuming a hypothetical series of liquids which have no polar surface energy component, so that $\gamma_L = \gamma_{LD}$.

and $\gamma_S D$ for paraffin is 25.5 dynes/cm. (13), and from the relationship (10):

$$\gamma_L = \gamma_{LD} + \gamma_{LP} \quad (\text{Eq. 3})$$

where γ_{LP} is the polar force component of the surface tension. It is assumed that only dispersion forces are operative between paraffin and the liquid series (13). Table II shows the results of these calculations. It can be seen that dispersion components of the series do not vary greatly throughout the entire surface tension range, while the polar component varies considerably. When relating these results to Fig. 1, it is apparent that high contact angles on human excised skin are observed when the water–acetone mixtures have large polar energy contributions to the total surface tension. Thus, it appears that the skin surface has little interaction with polar forces of the liquids under investigation.

Figure 2 is a critical surface tension conversion plot from which, according to the method of Dann (10), $\gamma_S D$ for skin is determined in the following manner.

If γ_C is defined as the point where $\cos \theta$ equals 1 for a particular liquid series on a particular surface, then at this point Eq. 1 can be given as:

$$1 = -1 + 2\sqrt{\gamma_S D} \frac{\sqrt{\gamma_{LD}}}{\gamma_L} \quad (\text{Eq. 4a})$$

Table III—Comparison of Observed Contact Angles on Live Skin and Calculated Values Using the GGFY Equation*

Compound	γ _L , dynes/cm.	γ _{LD} , dynes/cm.	θ Observed, degrees	θ Calculated, degrees
Water	72.0	22.0	108 ± 4	102
Glycerol	62.2	30.4	86 ± 3	85
Formamide	58.2	32.0	79 ± 7	79
Diiodomethane	50.6	50.6	55 ± 7	45
Tetrabromoethane	49.7	49.7	42 ± 5	43
Ethylene glycol	47.6	27.1	70 ± 5	71
Benzyl alcohol	39.2	34.9	41 ± 5	34
Tetrachloroethane	36.1	36.1	0	0
Mineral oil	31.9	31.9	0	0
Decahydro-naphthalene	30.8	30.8	0	0

* Results are quoted ± SD of the parameter.

Table IV—Comparison of Observed and Calculated Contact Angles on Skin for Liquids Having Poorly Determined γ_{LD} Values^a

Liquid	γ_L , dynes/ cm.	γ_{LD}^b , dynes/ cm.	θ	θ	θ
			Observed, Excised Skin, degrees	Observed, Live Skin, degrees	Calcu- lated ^c , Skin, degrees
α -Bromo- naphthalene	44.5	66.4	43 \pm 1.4	44 \pm 4.4	34
Acetophenone	39.2	44.5	47 \pm 5.1	47 \pm 5.6	20
Chlorophenyl- benzene	41.7	56.4	37 \pm 4.6	43 \pm 5.8	28

^a Results are quoted \pm SD of the parameter. ^b From contact angles on paraffin and Eq. 2. ^c From Eq. 1 using $\gamma_{SD} = 37.0$ dynes/cm. for skin and assuming $\gamma_{LD} = \gamma_L$ for all liquids.

or:

$$\frac{\sqrt{\gamma_{LD}}}{\gamma_L} = \frac{1}{\sqrt{\gamma_{SD}}} \quad (\text{Eq. 4b})$$

Since by definition at γ_C the value of γ_L equals γ_C , the curves in Fig. 2 were obtained by plotting γ_L versus $\sqrt{\gamma_{LD}}/\gamma_L$. Curve A in Fig. 2 was constructed using γ_L and γ_{LD} values obtained for the acetone-water series on paraffin as shown in Table II. Curve B in Fig. 2 represents a hypothetical liquid series of pure hydrocarbons having only dispersion energies so that $\gamma_L = \gamma_{LD}$. To obtain γ_{SD} for skin, pass a vertical line through curve A at the point where γ_C is 27.5 dynes/cm., the measured value of γ_C for skin using the acetone-water series. Where the line intercepts curve B is the expected value of γ_{SD} for skin, since for the hypothetical liquid series of pure hydrocarbons γ_C is equal to γ_{SD} . The γ_{SD} for skin was equal to 37 dynes/cm. Thus, nonpolar liquids ($\gamma_{LP} = 0$) having surface tensions less than 37 dynes/cm. should completely wet skin.

Using Eq. 1, with the stated assumptions, values of contact angles on skin were calculated for several organic liquids (Table III). Values of γ_{LD} for each liquid were determined by contact angle measurements on paraffin and use of Eq. 2. Contact angles of each liquid were measured on human skin and, as shown in Table III, the agreement between the measured and calculated angles is satisfactory.

The accuracy of the determination of γ_{LD} values will determine the accuracy of calculated θ values. In some cases, wide variations between calculated and observed θ values for liquids on skin were observed. Table IV shows poor agreement between calculated and observed θ values for α -bromonaphthalene, acetophenone, and chlorophenylbenzene⁴ on skin. For these liquids it is seen that γ_{LD} values determined from contact angles on paraffin and Eq. 2 are greater than γ_L values. This is due to the chemical or physical interaction between the liquid and the paraffin surface. Thus, it is

⁴ A mixture of 2-chloro-, 3-chloro-, and 4-chlorophenylbenzene (Araclor 1232, Applied Science Laboratories, State College, Pa.) was used.

clear that reliable γ_{LD} values are essential for the proper use of the GGFY equation.

CONCLUSIONS

The results of these studies strongly indicate that little, if any, polar interaction occurs between liquids and clean skin surfaces. The hydrophobic nature of the skin surface is in agreement with the work of Ginn *et al.* (8) and Adamson *et al.* (7). Additionally, the GGFY equation as described by Dann satisfactorily predicts contact angles of liquids on human skin.

A possible explanation of the hydrophobicity of skin is that polar groups present in the α -keratin structure of the stratum corneum are oriented away from the skin-air interface. Scheuplein's (14) hypothesis that detergents may uncoil and extend the α -keratin structure suggests that the coiled, unextended structure could be such that polar groups are inaccessible for polar interactions with liquids in the wetting process.

In summary, it was shown that the GGFY equation satisfactorily describes wetting of skin by several liquids if accurate γ_{LD} values are employed. The observed hydrophobic nature of the skin surface can be attributed to polar groups oriented away from the skin surface.

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