NRL Report 648

AD 646869

Critical Surface Tension for Spreading on a Liquid Substrate

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January 17, 1967

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH

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Washington, D.C.

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ABSTRACT

A plot of the initial spreading pressures (F_{ba}) or initial spreading coefficients (S_{ba}) against the surface tensions of a homologous series of organic liquids b can be used to determine the critical surface tension for spreading (γ_c) on a second substrate liquid phase a. Straight-line relations are found for various homologous series. The intercept of that line with the axis of abscissas ($F_{ba} = 0$, or $S_{ba} = 0$) defines a value of γ_c for that series. This method is advantageous because it eliminates the need for measuring (or calculating) the contact angle of lens b floating on liquid a, it can be applied to any liquid substrate, and it is applicable even when γ_c does not lie within the range of surface tensions of the members of the homologous series of liquids b. The value of γ_c for the water/air interface has been determined in this way using several homologous series of pure hydrocarbon liquids. The lowest value found was 21.7 dynes/cm at 20°C for the n-alkane series. Higher γ_c values were obtained using olefins or aromatic hydrocarbons as the result of interaction between the unsaturated bond and the water surface. Since the results are analogous to those reported earlier for solid surfaces, it is concluded that the clean surface of water behaves as a low-energy surface with respect to low-polarity liquids. This result is to be expected if only dispersion forces are operative between each alkane liquid and water.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C02-21
ONR Project Order P0-6-0035
Subproject RR 001-02-01

Manuscript submitted September 13, 1966.

CRITICAL SURFACE TENSION FOR SPREADING ON A LIQUID SUBSTRATE

INTRODUCTION

The concept of a critical surface tension for spreading (γ_c), originally developed from experiments on solid surfaces (1), was demonstrated by Jarvis and Zisman (2) to be applicable also to characterize the surface properties of liquids. For example, all members of a series of liquid fluoroesters with surface tensions of 19.7 dynes/cm or less were able to spread spontaneously on a liquid alkyl polyether substrate having a surface tension of 23.0 dynes/cm at 20°C, whereas those with surface tensions of 20.7 dynes/cm or more did not spread. Therefore, they estimated that the polyether surface had a value of γ_c midway between 19.7 and 20.7 dynes/cm. The largest value of γ_c determined for any liquid investigated by them was 29.0 dynes/cm for an aliphatic diester whose surface tension at 20°C was 30.1 dynes/cm. Since all of the fluorinated compounds, including those with surface tensions as high as 31.1 dynes/cm, spread on substrate liquids whose surface tension was 35.9 dynes/cm or higher, γ_c could not be determined for these substrate liquids. Thus, the method of Jarvis and Zisman was applicable only when a homologous series of spreading liquids could be found such that at least one member had a surface tension greater than the critical surface tension of the liquid substrate being investigated.

Johnson and Dettre (3) recently determined the critical surface tensions of several liquid fluorinated alcohols and of water. Their approach was to measure the surface and interfacial tension and with them to calculate the equilibrium contact angle (θ) of each of the n-alkane liquids by means of the Young equation. From a plot of $\cos\theta$ vs the alkane surface tension (γ_b), they obtained a value of γ_c of 19.1 dynes/cm for a clean water surface at 24.5°C.

A much more convenient method of measuring the value of γ_c of the surface of liquid a is based on a plot of the initial spreading coefficient (S_{ba}) of liquid b on liquid a vs γ_b, the surface tension of liquid b, where b is a member of a homologous series of pure organic liquids. This method has two advantages over the preceding methods: first, it eliminates measuring (or calculating) the contact angle of a drop of liquid b in the presence of the deforming and obscuring meniscus of the substrate liquid a; second, it does not require that γ_c of liquid a should fall within the range of surface tensions exhibited by the collective members of the series of homologous spreading liquids. A recent report by Pomerantz, Clinton, and Zisman (4) has made available a rapid and reliable method for measuring S_{ba} from the initial spreading pressure F_{ba} for any liquid b which is able to spread spontaneously on a; in addition, they also have supplied a substantial amount of data on the spreading properties on water of many pure hydrocarbons.

By analogy with the results of past investigations of this Laboratory on liquid spreading upon solid substrates (1), each homologous series of spreading liquids would be expected to define a critical surface tension for spreading which should be a characteristic of the surface of liquid substrate a. When the interaction between liquid b and substrate liquid a arises solely from London dispersion forces, the critical surface tension of wetting would be the same, regardless of the homologous series used to supply the spreading liquid b. It is this common minimum value of γ_c in which we are most interested here. If liquid b adheres to a by other forces, such as hydrogen bonding, then that homologous series of b liquids would define a higher value of γ_c. We would expect graphs of S_{ba} vs γ_b to be a series of lines, one for each homologous series, with each line displaced from the other by an amount which would be a measure of the contribution to the liquid/liquid adhesion arising from forces other than the dispersion forces. If the intercept at $S_{ba} = 0$ for any one curve is used to determine γ_c, then γ_c would be greater, the stronger the nondispersion forces of adhesion.

If we desire to obtain the minimum possible intercept on the line $S_{ba} = 0$, we should use a homologous series of spreading liquids, no member of which has the ability to form either ionic or hydrogen bonds with the molecules in the surface of the liquid a. Hence when liquid substrate a is water, it is essential that liquid b should not ionize or form hydrogen bonds with water. Because there is much evidence for the hydrophilic character of the unsaturated carbon-carbon bond (4,5) and for its hydrogen-bonding ability (6), it is necessary to avoid unsaturated compounds and to use only the saturated hydrocarbons to determine the minimum value of γ_c for water.

SPREADING OF THE ALKANES ON WATER AND RELATION TO γ_c

Since the surface tension of water much exceeds that of any organic liquid, it might be expected that organic liquids would always spread spontaneously over the clean surface of water. Nevertheless, many pure organic liquids, including numerous hydrocarbons, do not spread on water but form, instead, nonspreading lenses (7-9). As all of the n-alkanes below nonane spread spontaneously on water at 20°C (4,7,10), γ_c for water must lie between 21.8 and 22.9 dynes/cm, since these are the surface tensions of n-octane and n-nonane (11). A more precise determination of γ_c can be obtained if we plot S_{ba}, the initial spreading coefficient on water, as a function of γ_b for the n-alkane family of liquids. Until recently the only way to obtain S_{ba} was from the equation by which it was defined by Harkins (7-9), i.e.,

$$S_{ba} = \gamma_a - (\gamma_b + \gamma_{ab}). \tag{1}$$

When liquid b is nonspreading, it still is necessary to compute S_{ba} from Eq. (1). But when b spreads spontaneously on a, a much simpler approach is now available, because S_{ba} is usually equal to the initial spreading pressure (F_{ba}) (4,10), which, in turn, can be measured conveniently by the "piston monolayer" method of Washburn and Keim (12). This method has several advantages, one of which is that only a few drops of pure liquid b are needed; a second is its lower sensitivity to the presence of impurities, as compared to interfacial tension measurements. This characteristic is well illustrated by the identical values of S_{ba} obtained seven years apart by two independent observers using different film balances, new sources of alkanes, and different methods of purification (4).

In Fig. 1 is a plot of S_{ba} vs γ_b for the lower n-alkanes on water at 20°C. These values of S_{ba} were obtained from Table 2 of Ref. 4. It will be seen that S_{ba} intercepts the axis $S_{ba} = 0$ at $\gamma_b = 21.9$ dynes/cm, which therefore is the value of γ_c for water at 20°C. Figure 2 is an analogous plot for the nonspreading members of the n-alkane family of liquids, based on the literature values of S_{ba} at 20°C shown in Table 1. A value of $\gamma_c =$ 21.5 dynes/cm can be determined by the intercept with the line $S_{ba} = 0$. A straight line provides a good fit to the data of Aveyard and Haydon (13) for S_{ba} vs γ_b for the four nonspreading, higher n-alkane homologs shown in Fig. 2, even though some curvature would be noted in a plot of their interfacial tension values as a function of N, the number of carbon atoms, for the series of alkanes from n-pentane through n-hexadecane.

Because a plot of S_{ba} vs γ_b should, in principle, be obtainable for some homologous series of organic liquids on any liquid substrate, we have at hand a general method of measuring γ_c for every liquid substrate. In practice the spreading pressure method is limited by the problem of finding a suitable piston monolayer for the particular liquid substrate. That the method is not restricted to the determination of γ_c for water is

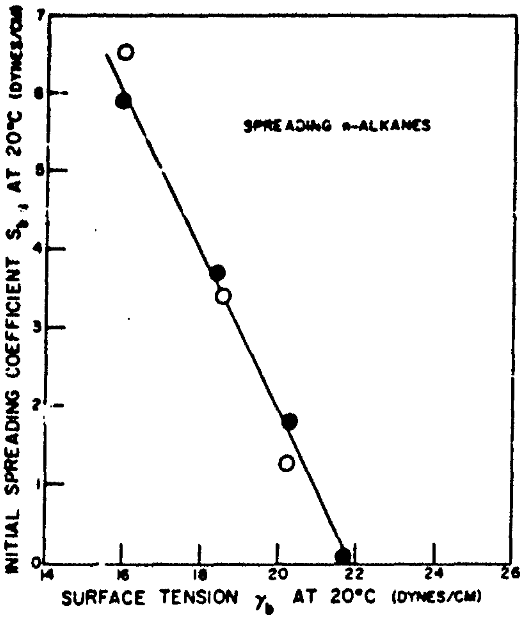

Fig. 1 - The initial spreading coefficient (S_{ba}) as a function of the surface tension (γ_b) of n-alkanes which spread on water. Filled symbols indicate data from Pomerantz, Clinton, and Zisman (4); open symbols indicate data from Aveyard and Haydon (13).

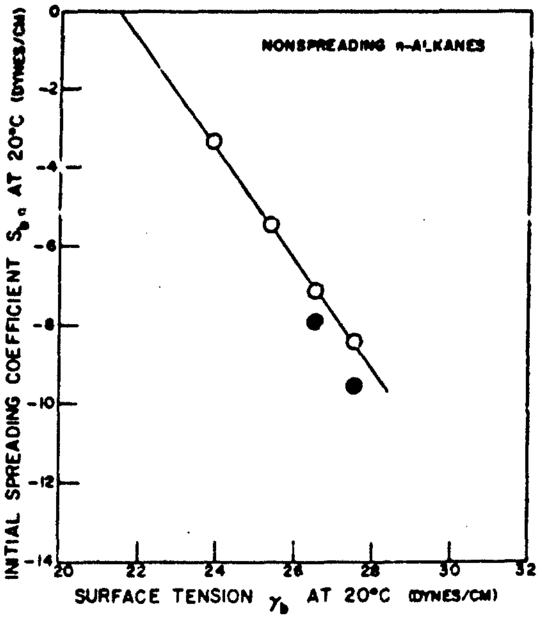

Fig. 2 - The initial spreading coefficient (S_{ba}) as a function of the surface tension (γ_b) of n-alkanes which do not spread on water. Open symbols indicate data from Aveyard and Haydon (13); filled symbols indicate data from Harkins (14).

evident from the investigation of Ellison and Zisman (19) in which values of S_{ba} were measured for an ethoxy-end-blocked silicone, two partially fluorinated organic silicates, and isopropanol when spreading on white mineral oil. A fluorochemical piston monolayer and an all-Teflon film balance were used.

The effect of branching in the hydrocarbon liquid on the value of γ_c for water was investigated by using other groups of homologous saturated hydrocarbons. Figure 3 is a plot made with the data obtained from Ref. 4. Note that all seventeen data points for the branched alkanes are displaced only slightly from those of the n-alkanes and that all but two of the points are well described by a straight line intercepting the zero axis of abscissas at γ_c = 22.5 dynes/cm. As would be expected from the fact that the reversible work of adhesion for methyl groups is slightly larger than that of methylene groups (4), the data points closest to those of the unbranched alkanes are those of the branched alkanes containing the fewest methyl groups per molecule.

No case of spreading on water at ordinary temperature has been reported for any pure, saturated cyclic hydrocarbon (naphthenic), although at least fourteen naphthenics have been observed. Thus, using the Washburn and Keim method, Clinton (20) found negative spreading pressures for two homologous series of pure naphthenics (cyclopentane through n-butylcyclopentane and cyclohexane through n-butylcyclohexane). Lens formation has been reported for isopropyl bicyclohexyl and dicyclohexyl (21). Since the lowest value of γ_b for any of these compounds is 22.2 dynes/cm at 20°C found for methylcyclopentane by Robinson (22), it is apparent that γ_c must be less than 22.2 dynes/cm for this series of liquids. Reported values of S_{ba} of -8.54 and -11.17 dynes/cm (15) and of γ_b of 29.89 and 32.18 dynes/cm (23) for the cis and trans isomers of decahydronaphthalene, respectively, are consistent with this value of γ_c. This result is in good agreement

Table 1
Spreading Pressures and Related Properties for Various Hydrocarbons on Water
(Data at 20°C unless otherwise specified)

Hydrocarbon	Surface Tension γ_b (dynes/cm)	Spreading Pressure F_{ba} (dynes/cm)	Spreading Coefficient S_{ba} (dynes/cm)	Interfacial Tension γ_{ab} (dynes/cm)
n-Alkanes				
n-Nonane	22.92 (11)	<0 (4)		
n-Decane	23.92 (11)	<0 (4)	-3.35 (13)	52.30 (13) 51.24 (15) 52.30 (16) 52.0 at 24.5°C (3)
n-Dodecane	25.4 (11)	<0 (4)	-5.41 (13)	52.78 (13) 52.8 at 24.5°C (3)
n-Tetradecane	26.53 (11) 25.6 (17)	<0 (4)	-7.11 (13) -7.93 (14)	53.32 (13) 54.17 (14) 52.2 (17) 48.4 at 25°C (18)
n-Hexadecane	27.52 (11)	<0 (4)	-8.44 (13) -9.56 (14) -9.52 (9, p. 104)	53.77 (13) 54.84 (14) 53.3 at 24.5°C (3)
Aromatics				
t-Butylbenzene	27.63 at 25°C (10)	5.3 (10)	5.2 (10)	39.3 at 25°C (10)
iso-Propylbenzene	27.71 at 25°C (10)	6.0 (10)	5.7 (10)	38.7 at 25°C (10)
sec-Butylbenzene	28.20 at 25°C (10)	4.7 (10)	4.7 (10)	39.2 at 25°C (10)
1,2,3,4-Tetrahydronaphthalene	36.02 at 25°C (10)	0.0 (10)	-2.5 (10)	38.6 at 25°C (10)

with the values of γ_c calculated previously for the n-alkane liquids. For the remainder of this discussion, we will assume γ_c = 22.0 dynes/cm with respect to low-polarity liquids.

EFFECT OF UNSATURATED BONDS ON γ_c

As shown in Fig. 3, the introduction of unsaturation at the α-position in the straight-chain alkanes resulted in a rectilinear graph of S_{ba} vs γ_b with almost the same slope as that exhibited by the n-alkanes but with an intercept of γ_c = 25.1 dynes/cm. The difference of 25.1 - 21.7 = 3.4 dynes/cm is presumably a measure of the contribution to the observed

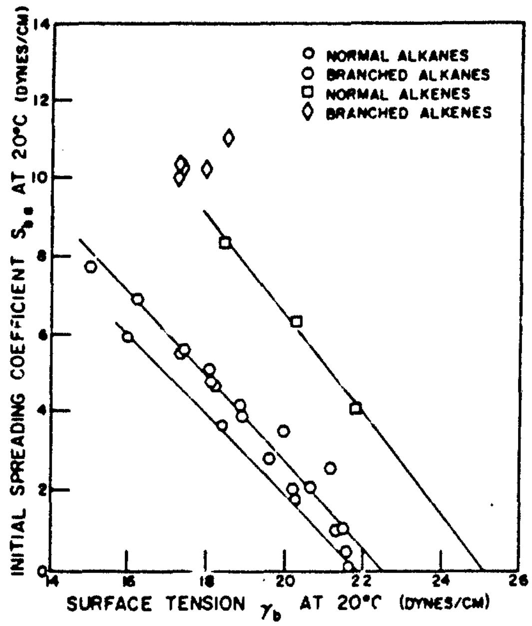

Fig. 3 - The effect of branching and unsaturation on the initial spreading coefficient (S_{ba}) as a function of the surface tension (γ_b) of acyclic hydrocarbons. All data are from Pomerantz, Clinton, and Zisman (4).

liquid/liquid adhesion resulting from forces between the water and olefinic double bond other than the dispersion forces. Pomerantz, Clinton, and Zisman (4) found by similar reasoning a difference of 4.2 dynes/cm representing the contribution of the double bond to S_{ba} when saturated and unsaturated hydrocarbons of the same boiling point range were compared.

The distribution of data points for the unsaturated branched alkanes in Fig. 3 is consistent with a straight-line relation but is not sufficient to determine its intercept with the axis of abscissas. A comparison of the relative positions of the data points for a saturated branched alkane and two related unsaturates, 2-methyl-pentane compared to 2-methyl-1-pentene and 4-methyl-1-pentene (see Tables 2 and 3 of Ref. 4), suggests that unsaturation in the branched alkanes may increase the apparent value of γ_c by 5 dynes/cm.

The effect of aromatic and olefinic unsaturation on γ_c can be compared, and for this purpose use was made of the data on the n-alkyl benzenes in Tables 3 and 4 of Ref. 4. A graph of the value of S_{ba} vs γ_b was of no help in calculating γ_c, because γ_b varied too little in this series of compounds. However, a graph of S_{ba} versus the number of carbon atoms in the alkyl chain revealed that S_{ba} approaches zero at the homolog n-hexyl benzene; hence γ_c must be about equal to γ_b for n-hexyl benzene or about 30 dynes/cm. When additional phenyl groups were present in the liquid molecule, γ_c was even higher. Among the hydrocarbons containing more than one phenyl group, liquids with surface tensions as high as 37 dynes/cm have been reported by Harkins and Feldman (7) to exhibit initial spreading prior to lens formation, as well as small positive spreading coefficients. The increase in γ_c of some 7 or more dynes/cm upon the introduction of a second phenyl group is consistent with the value of about 8 dynes/cm resulting from the introduction of the first phenyl group.

A comparison of the spreading behavior on water of cyclohexane (F_{ba} = -3.2 dynes/cm at 20°C (15)) and of benzene (Table 4 of Ref. 4) is revealing. Cyclohexane (γ_b = 24.95 dynes/cm at 20°C (11)) is nonspreading on water and it belongs to the group of naphthenic liquids for which γ_c of water is 22 dynes/cm. The surface tension of benzene (28.88 dynes/cm at 20°C) exceeds that of its saturated counterpart by 3.9 dynes/cm and exceeds the minimum value of γ_c of water (21.7 dynes/cm average for unbranched, saturated hydrocarbons) by 7.2 dynes/cm; nevertheless, benzene spreads spontaneously over water and has a large positive value of S_{ba}. The difference in S_{ba} for these two liquids is 13.0 dynes/cm, although their liquid surface tensions differ by only 3.9 dynes/cm. A comparison of the interfacial tension for the system benzene/water (34.1 dynes/cm (4)) with that for cyclohexane/water (51.0 dynes/cm(10)) reveals a difference in γ_{ab} of 16.9 dynes/cm, which is about four times as large as that for the systems hexene-1/water vs hexane/water (46.0 vs 50.8 dynes/cm (4)). Therefore, the decrease in γ_{ab} upon introduction of the resonating aromatic system of three double bonds was approximately four times that caused by the introduction of one alpha olefinic double bond.

Comparison of the data given previously for decahydronaphthalene (15,23) and in Table 1 for 1,2,3,4-tetrahydronaphthalene indicates that the substitution of an aromatic for a saturated ring in one half of a fused ring system is sufficient to increase γ_c by 12 dynes/cm, if it is assumed that the data point for the nonspreading aromatic compound falls on a line with the same slope as that for the nonspreading naphthenic hydrocarbons. In this case, however, the difference in γ_{ab} corresponds to 13 dynes/cm or less when aromaticity is introduced in the condensed ring compound. It is no surprise that the effect of aromaticity on γ_c is not uniquely determinable, since the forces additional to dispersive forces will depend not only on the number of aromatic rings present, but also on the ease with which the aromatic ring can orient with its plane face parallel to and in contact with the surface of the water at one extreme or with the aromatic ring of an adjacent organic molecule at the other extreme. Thus, steric considerations must influence the interaction of the aromatic ring with the substrate.

GENERAL REMARKS

Table 2 summarizes the values of γ_c for water and other liquid substrates obtained by the several methods employed to date. Our value of γ_c of 22 dynes/cm for water is consistent with all the results obtained for the three types of organic liquids which have low polarity and are not capable of interacting through hydrogen bonding with the underlying water surfaces, i.e., n-alkanes, branched alkanes, and naphthenics. Thus, bulk water is shown to be a low-energy surface when the organic liquids are limited to those which only have dispersion forces operating to make them adhere to the water surface. Moreover, the value of $\gamma_c = 22$ dynes/cm is in accord with the calculated dispersion component $\gamma^d = 21.8 \pm 0.7$ dynes/cm obtained by Fowkes (24) for the surface of bulk water at 20°C. This agreement is significant, since it is tantamount to stating that the surface field of force of bulk water can be treated as comprising only an additive dispersion energy and a hydrogen-bonding energy contribution. Johnson and Dettre's significantly lower value of $\gamma_c = 19.1$ dynes/cm at 24.5°C (3) is difficult to explain, since one would not expect the 4.5°C increase in temperature to cause such a decrease in γ_c. Indeed, the temperature coefficients of γ_b and γ_{ab} reported by Aveyard and Haydon (13) indicate a decrease in γ_c of only 0.7 dyne/cm for a 10°C rise in temperature.

The experimental basis for the straight-line relationship obtained between S_{ba} and γ_b for the clean surface of water is the near constancy of γ_{ab} and the nearly linear behavior of γ_b for the homologous families of alkanes, 1-alkenes, and n-alkyl benzenes, when N is not too large. This experimental independence of γ_{ab} from γ_b has been established by many measurements on liquid/liquid systems and is illustrated by Figs. 3 and 4 of Ref. 4. A straight-line relation would be expected, since S_{ba} is equal to the difference between the reversible work of adhesion (W_{ba}) and the work of cohesion (W_{bb}). The first term is proportional to N, provided the adsorbed hydrocarbon molecules lie in the plane of the water surface, and the second term is also linearly related to N when N is not large.

The evidence presented here for the low-energy character of the surface of liquid water with respect to low-polarity liquids is in agreement with results reported by us recently (21) on the effect of increased water vapor adsorption on glass in reducing its wettability by hydrophobic organic liquids and its critical surface tension (γ_c). It was

Table 2
Comparison of the Critical Surface Tension for Spreading (γ_c) with the Liquid Surface Tension (γ_a) for Various Low-Energy Liquids

Substrate Liquid	Temp. (°C)	Surface Tension γ_a (dynes/cm)	Critical Surface Tension γ_c (dynes/cm)	Ref.
$F(CF_2)_2CH_2OH$	24.5	17.4	13.2	3
Ucon fluid DLB 44E (a double end-blocked polypropylene oxide)	20	23.0	20.2	2
$H(CF_2)_4CH_2OH$	24.5	23.8	17.5	3
$H(CF_2)_2CH_2OH$	24.5	26.0	17.8	3
n-Hexadecane	20	27.3	23.1	2
Mineral oil (light petrolatum)	20	29.9	23.8	2
Squalene	20	31.4	26.7	2
Bis(2-ethylhexyl)sebacate	20	30.1	29.0	2
Nitromethane	20	35.9	>31.1	2
Alkazene 42 (1,2-dibromoethylbenzene)	20	38.3	>31.1	2
1-Methylnaphthalene	20	38.4	>31.1	2
Tricresyl phosphate	20	40.4	>31.1	2
Propylene carbonate	20	41.0	>31.1	2
Phosphen 4 (a phenoxy bis(o-chlorophenoxy)phosphate)	20	43.5	>31.1	2
Aroclor 1248 (a trichlorobiphenyl)	20	43.7	>31.1	2
Water	24.5 20	72.1 72.8	19.1 21.7	3 This report

found that γ_c decreased markedly during the formation of the first adsorbed monolayer of water and reached a minimum value at a duplex film which, in turn, was somewhat above the value of γ_c for bulk water given here.

The fact that γ_c is as low as 22 dynes/cm for the alkanes spreading on water deserves interpretation in terms of the surface structure of water. Obviously, when water is in contact with an alkane or other nonhydrogen-bonding liquid, the molecules of water in the interface will be oriented to make the free surface energy a minimum. The highly associated nature of liquid water makes it difficult to determine that surface configuration. It is surely not the result of the oriented adsorption of monomeric water.

Stevenson (25) has concluded from infrared absorption data that fewer than 1% of the molecules of liquid water at ordinary temperatures exist in a nonhydrogen-bonded state. Timmons and Zisman (26) have recently shown that liquid water at 20°C behaves in contact angle hysteresis experiments as if it were comprised on the average of aggregates of six monomers. It is suggested that the adsorbed species at the alkane/water interface is comprised of these or similar associated clusters so organized and oriented as to minimize the surface energy. It is interesting that Adamson and Dormant (27) have recently reported that ice acts like a low energy surface with respect to the adsorption of nitrogen at 78°K, and they have concluded that the hydrogen atoms in the ice surface are outermost and are not in the relatively polar form of hydroxyl groups.

The value of 22 dynes/cm for the critical surface tension of water is much less than the surface tension of water (72.8 dynes/cm at 20°C). While γ_c must correlate with (be symbatic with) the surface energy γ_a of a liquid, or γ_{S° of a solid, the above result again emphasizes what has been carefully pointed out previously by Fox and Zisman (28), namely, that it is not valid to equate γ_c to γ_{S°. That this admonition is equally applicable to liquid surfaces (whether organic or aqueous) is illustrated by the tabulation of γ_c and γ_a values from the literature in Table 2.

Moreover, since the surface energy can be determined experimentally for a liquid, the extent to which γ_c is not a measure of the surface energy can be shown graphically, as in the plot of γ_c vs γ_a in Fig. 4. Here the dotted construction line (line B) indicates

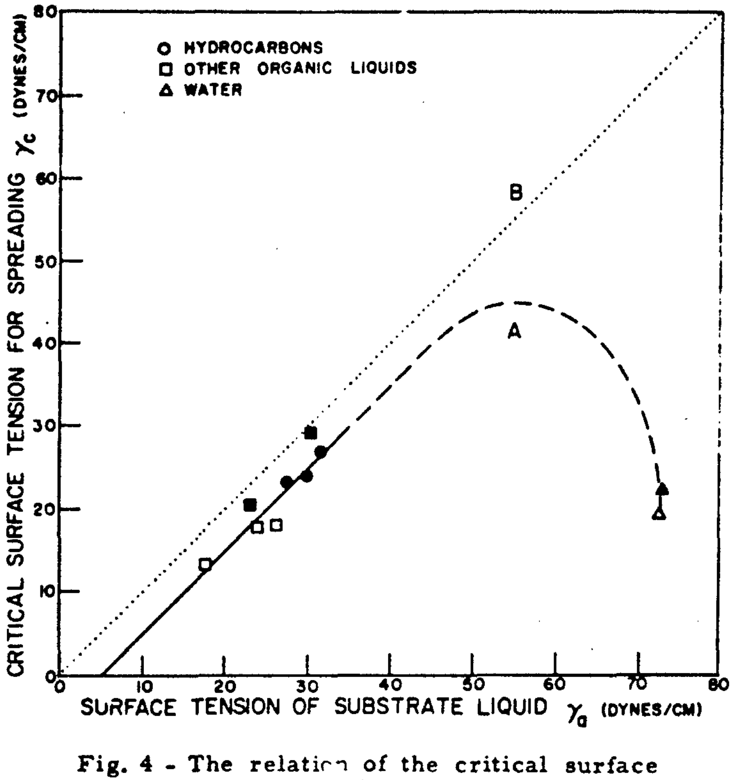

Fig. 4 - The relation of the critical surface tension for spreading (γ_c) to the surface tension (γ_a) of the substrate liquid. Filled symbols indicate data at 20°C from this report and from Jarvis and Zisman (2); open symbols indicate data at 24.5°C from Johnson and Dettre (3).

what the relation would be if γ_c were equal to the free surface energy or surface tension (γ_a). The relation determined experimentally is indicated by the data points representing the results for the several liquids at either 20°C or 24.5°C as given in Table 2; since the temperature difference is small, it is not expected to affect the results significantly. From the positions of the data points for the three hydrocarbon liquids relative to line B, it is apparent that the dispersion energy γ^d (as measured by γ_c) represents a major fraction of the free surface energy of these compounds; similar considerations apply to the remaining five organic liquids. In the case of water, however, γ^d (as measured by the minimum value of γ_c) is a much smaller fraction of the free surface energy, and the difference is presumed to be the contribution arising from hydrogen-bonding energy between adjacent water molecules. Thus, when values of γ_c greater than the minimum value are obtained (for different liquid series on water), the excess must represent the net effect of both the change of forces operating across the interface (due to dipole-dipole interaction, increased induced polarization, hydrogen-bonding, etc.) and the alteration of forces between the adjacent water molecules (due to molecular reorientation, variation in cluster size, etc.).

Figure 4 suggests that the data point for water could be connected to those for the organic liquids by a curve (such as curve A) which recedes away from line B the greater the nondispersion-force contribution to the surface free energy. Since hydrogen bonding is prevalent in most organic liquids having surface tensions above 50 dynes/cm, a portion of curve A has been dashed in to suggest the relation for such liquids; the continuous portion of the curve indicates the relation determined experimentally for liquids of surface tensions below about 30 dynes/cm. Experimental data on γ_c for liquids of high surface tension and strong hydrogen bonding are needed; the data in Table 2 for liquids with surface tensions above 30 dynes/cm indicate that such a determination is experimentally feasible.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Naval Research Laboratory
Washington, D.C. 20390

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
CRITICAL SURFACE TENSION FOR SPREADING ON A LIQUID SUBSTRATE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
An interim report on a continuing problem.

5. AUTHOR(S) (First name, middle initial, last name)
Elaine G. Shafrin and W. A. Zisman

6. REPORT DATE January 17, 1967	7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 28

8a. CONTRACT OR GRANT NO.
NRL Problem C02-21
b. PROJECT NO.
ONR Project P0-6-0035
c.
Subproject RR 001-02-01
d.

9a. ORIGINATOR'S REPORT NUMBER(S)
NRL Report 6488

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Department of the Navy (Office of Naval Research), Washington, D.C. 20390

13. ABSTRACT

A plot of the initial spreading pressures (F_{ba}) or initial spreading coefficients (S_{ba}) against the surface tensions of a homologous series of organic liquids b can be used to determine the critical surface tension for spreading (γ_c) on a second substrate liquid phase a. Straight-line relations are found for various homologous series. The intercept of that line with the axis of abscissas ($F_{ba} = 0$, or $S_{ba} = 0$) defines a value of γ_c for that series. This method is advantageous because it eliminates the need for measuring (or calculating) the contact angle of lens b floating on liquid a, it can be applied to any liquid substrate, and it is applicable even when γ_c does not lie within the range of surface tensions of the members of the homologous series of liquids b. The value of γ_c for the water/air interface has been determined in this way using several homologous series of pure hydrocarbon liquids. The lowest value found was 21.7 dynes/cm at 20°C for the n-alkane series. Higher γ_c values were obtained using olefins or aromatic hydrocarbons as the result of interaction between the unsaturated bond and the water surface. Since the results are analogous to those reported earlier for solid surfaces, it is concluded that the clean surface of water behaves as a low-energy surface with respect to low-polarity liquids. This result is to be expected if only dispersion forces are operative between each alkane liquid and water.

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Critical surface tension						
Filament wound construction						
Glass textiles						
Fibers						
Plastics						
Water						
Surface properties						
Organic compounds						
Liquids						
Spreading						
Hydrocarbons						
Alkenes						
Alkanes						
Surface tension						
Hydrogen bonding						
Adhesion						
Structure of water						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

Security Classification