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Spreading Pressure, Interfacial Tension, and Adhesional Energy of the Lower Alkanes, Alkenes, and Alkyl Benzenes on Water

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SPREADING PRESSURE, INTERFACIAL TENSION, AND ADHESIONAL ENERGY OF THE LOWER ALKANES, ALKENES, AND ALKYL BENZENES ON WATER

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INTRODUCTION

In 1940 Washburn and Keim (1) reported a simple and sensitive method for determining the spreading pressure on water of any spontaneously spreading organic liquid compound. Their method, which is a logical extension of the "indicator" or "piston oil" technique of Cary and Rideal (2) and Langmuir and Schaefer (3), used a monomolecular adsorbed film of a water-insoluble, nonvolatile, surface-active compound such as stearic acid, palmitic acid, or tristearin to function as a "piston film" on water for transmitting surface pressure. A small drop of the liquid whose spreadability was being measured was placed in the middle of the area covered by the insoluble piston monolayer, where it formed a floating lens. As the liquid lens spread, the pressure it created was transmitted to the floating barrier of a Langmuir-Adam film balance. The film balance was adjusted by means of the floating and sliding barriers until the piston film allowed the spreading lens to become thin enough to be a duplex film, i.e., such that gravitational effects in the lens did not affect the film pressure. At that stage a slight displacement of the sliding barrier would expand or contract the thin lens without altering the film pressure indicated by the floating barrier. The observed constant pressure is defined as the "spreading pressure" on water of that liquid. Ellison and Zisman (4) demonstrated that the piston monolayer method could be adapted to measuring the spreading pressure of compounds on organic liquid substrates.

The piston monolayer method is rapid, sensitive, and convenient. Important advantages are: (a) only one drop of the organic liquid is required for each measurement, (b) the method is so rapid that it allows a reliable measurement to be made on compounds as volatile as benzene and hexane, and (c) measurements of sufficient accuracy can be made with a simple, compact film balance such as the Cenco "Hydrophil" balance. Since only a few minutes are needed for measurement of the spreading pressure, undesirable effects on spreading properties arising from oxidation or other chemical changes in the organic liquid are much decreased; this is an especial advantage in research on the spreading properties of unsaturated hydrocarbons or other oxidation-susceptible compounds.

Washburn and coworkers (1,5,6) have pointed out that each of the pure volatile compounds investigated by them had a spreading pressure equal to the Harkins initial spreading coefficient. These compounds are: benzene, toluene, ethylbenzene, the isomeric propylbenzenes and butylbenzenes, 2,2,4-trimethylpentane, isoamyl chloride, acetophenone, and diethyl carbonate. The equality of the spreading pressure and the initial spreading coefficient for each of four organic compounds spreading on a hydrocarbon liquid substrate was subsequently demonstrated by Ellison and Zisman (4).

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THEORETICAL CONSIDERATIONS

Many years earlier Harkins and Feldman (7) had defined three stages of spreading of liquid b on liquid a and assigned to each a spreading coefficient. The "initial spreading coefficient" (S_{ba}) was that of pure liquid b on pure liquid a; the "semi-initial spreading coefficient" ($S_{b'a}$) was that of liquid b saturated with a on pure a; and the "final spreading coefficient" ($S_{b'a'}$) was of liquid b saturated with a on liquid a which had been saturated previously with b. Hence, these three quantities were defined as follows:

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

$$S_{b'a} = \gamma_a - (\gamma_{b'} + \gamma_{ab'}) \tag{2}$$

$$S_{b'a'} = \gamma_{a'} - (\gamma_{b'} + \gamma_{a'b'}). \tag{3}$$

Here the prime superscript means that the one liquid phase was saturated with the other. Thus, Eqs. (1), (2), and (3) made evident how each spreading coefficient was to be calculated from the appropriate values of the surface and interfacial tension.

A thermodynamic condition for the spontaneous spreading of b on a was shown by Harkins and Feldman to be that

$$S_{ba} > 0. \tag{4}$$

In order that liquid b would remain spread on a under the final condition of equilibrium between the two mutually saturated liquids and their vapors, it was also shown that

$$S_{b'a'} > 0. \tag{5}$$

By analogy with the definition of the three spreading coefficients, and in agreement with the ideas of Transue, Washburn, and Kahler (5) and Ellison and Zisman (4), three distinct spreading pressures also can be defined, each of which can be measured by the piston monolayer method. The first value will be called the "initial spreading pressure" (F_{ba}), the second the "semi-initial spreading pressure" ($F_{b'a}$); and the third the "final spreading pressure" ($F_{b'a'}$). These values refer respectively to: (a) the spreading pressure immediately after spreading the pure liquid b on substrate a as a thin lens in equilibrium with the piston film on clean liquid a, (b) the spreading pressure of a thin lens of liquid b saturated with a on the surface of pure liquid a, and (c) the spreading pressure of a thin lens of liquid b saturated with a on liquid substrate a which had been previously saturated with b. The last value ($F_{b'a'}$) should correspond to the equilibrium spreading pressure (F_e) of Cary and Rideal (2), provided that both liquids and their vapors formed an equilibrium system.

The agreement of the calculated values of S_{ba} with the spreading pressures of the volatile liquids (mostly hydrocarbons) reported by Washburn and coworkers (5,6), as well as the many hydrocarbons reported here, is ample evidence for concluding that the piston monolayer method does give for such liquids on water the initial spreading pressure (F_{ba}) rather than the semi-initial value ($F_{b'a}$). Because of the low mutual solubilities of the above-mentioned hydrocarbons and water and the fact that for them γ_b and γ_b are nearly equal, it is not astonishing that the observed spreading pressures by the rapid "piston film" method are the initial values.

A brief proof that F_{ba} must be equal to S_{ba} was given by Shewmaker, Vogler, and Washburn (6) by applying a simple thermodynamic argument based on the fact that the Harkins spreading coefficient is the surface free energy change resulting from the spreading process. The following discussion and thermodynamic argument are intended

to clarify matters and indicate the necessary assumptions and limitations in the proof that the observed surface pressure is equal to F_{ba} and also to S_{ba}.

Consider a spreading drop of pure liquid b resting on liquid a in equilibrium with an insoluble piston monolayer having a pressure of $\gamma_a - \gamma_{a*}$. Here γ_a is the surface tension of pure liquid a and γ_{a*} is the surface tension of liquid a covered with the piston monolayer. If the spreading lens is flat and thin so that gravity does not contribute significantly to the spreading pressure, then under surface pressure equilibrium conditions the lens can be expanded or contracted without the piston pressure being altered. Let the pressure exerted by the lens under these conditions be F_{ba}. We are assuming either that the measurement is rapid enough so that solution of a in b has not taken place or else that it does not make any difference, i.e., $F_{ba} = F_{b'a}$. Obviously, for equilibrium in the surface,

$$\gamma_a - \gamma_{a*} = \text{piston film pressure} = F_{ba} . \tag{6}$$

Let the sliding barrier be moved along the trough containing liquid a so that the area within the sliding barrier and floating barrier is decreased from A to $A - \Delta A$. The film pressure $(\gamma_a - \gamma_{a*})$ will remain unaltered, and the lens will contract by ΔA in order to maintain surface pressure equilibrium. Hence the surface area of liquid b at the gas/liquid interface will decrease by ΔA. The associated free surface energy will decrease by $\gamma_b \Delta A$, assuming liquid b has not been significantly altered by solution of a in b. Similarly, the area of the interface of liquids b and a will decrease by ΔA. The interfacial energy will decrease by the amount $\gamma_{ab} \Delta A$, assuming that γ_{ab} has not been altered by diffusion between liquids a and b. The movement of the sliding barrier will have decreased the size of the lens of liquid b, and it also will have increased (by the same amount) the area of liquid a which had not been covered by the piston film. In other words, the area occupied by the piston monolayer will remain constant because it is at constant film pressure and therefore is not altered in packing.

According to the second law of thermodynamics, the external work done on the system must be equal to the free energy increase. Hence,

$$(\gamma_a - \gamma_{a*}) \Delta A = (\gamma_a \Delta A) - (\gamma_b \Delta A) - (\gamma_{ab} \Delta A)$$

or

$$\gamma_a - \gamma_{a*} = \gamma_a - (\gamma_b + \gamma_{ab}). \tag{7}$$

However, $\gamma_a - (\gamma_b + \gamma_{ab}) \equiv S_{ba}$. Therefore,

$$\gamma_a - \gamma_{a*} = S_{ba} \tag{8}$$

and finally from Eq. (6)

$$F_{ba} = S_{ba} . \tag{9}$$

This thermodynamic argument is being applied to a system of liquids b and a under orientation and adsorption equilibrium. Subsequent changes by diffusion of molecules of a or b into the other liquid are considered to be much slower processes. An exactly analogous argument can be given for the system when sufficient time is taken in the measurement to allow molecules of a and b to diffuse across the interface to reach solubility equilibrium; on substituting $\gamma_{b'}$ for γ_b and $\gamma_{a'b'}$ for γ_{ab} in the preceding equations one then obtains

$$F_{b'a'} = S_{b'a'} . \tag{10}$$

Hence, the determination of which spreading pressure one measures by the piston monolayer method must be made on the basis of a knowledge of the time required for the measurement and the rate that solubility equilibrium is reached. In a rapid measurement with liquids which are not too soluble one measures F_{ba}. Then one can use the relation $F_{ba} = S_{ba}$. If the rate of diffusion of a into b is significant, one measures $F_{b'a}$. Often $F_{b'a} = F_{ba}$; hence one still obtains S_{ba}. In a slow enough process one obtains $F_{b'a'}$. If one can arrange to measure the spreading pressure rapidly to get $F_{b'a}$ and slowly to obtain $F_{b'a'}$, one can use the two results to calculate the equilibrium spreading pressure (F_e) by using the Harkins equation

$$F_e = F_{b'a} - F_{b'a'} . \tag{11}$$

The well-known Dupré relation states that

$$W_{ba} = \gamma_a + \gamma_b - \gamma_{ab} . \tag{12}$$

As Harkins showed, if the reversible work of cohesion of liquid b is W_{bb}, then it is given by

$$W_{bb} = 2\gamma_b . \tag{13}$$

From Eqs. (1), (12), and (13) the Harkins relation results:

$$W_{ba} - W_{bb} = S_{ba} . \tag{14}$$

Using Eqs. (13), (14), and (9), one can derive the useful relation

$$W_{ba} = 2\gamma_b + F_{ba} . \tag{15}$$

Furthermore, from Eqs. (15) and (12) there results the relation

$$\gamma_{ab} = (\gamma_a - \gamma_b) - F_{ba} . \tag{16}$$

That is, from measured values of F_{ba}, γ_a, and γ_b, one can compute both W_{ba} and γ_{ab}.

PURPOSE OF THE EXPERIMENTAL WORK REPORTED

While the values of γ_a and γ_b are readily measured, the equilibrium interfacial tension ($\gamma_{a'b'}$) is more difficult and time-consuming to obtain because it is highly sensitive to the traces of the hydrophilic organic impurities so often present. Therefore, it is now evident that the rapid measurement of the spreading pressure can furnish a convenient means of obtaining the initial value of the interfacial tension (γ_{ab}) and the value of the work of adhesion (W_{ba}), both of which are of much interest in surface chemistry. By slowing down the speed of the piston film method, one can arrange to measure $F_{b'a'}$ and not F_{ba} or $F_{b'a}$. In the experiments reported here Eq. (16) can be used to calculate γ_{ab}. This point will be discussed later when values of the interfacial tension obtained from Eq. (16) will be compared with experimental values of $\gamma_{a'b'}$.

The unsaturated carbon-carbon bond has been shown to be hydrophilic in character in many past studies of the film pressure on water vs area per adsorbed molecule. Well-known examples include oleic, linoleic, and linolenic acids as well as the corresponding unsaturated alcohols (8,9). Because of the absence of strongly hydrophilic groups in pure hydrocarbon liquids, however, investigations of their film-forming properties cannot be carried out with the Langmuir-Adam film balance by taking measurements of the film pressure (F) vs the area (A) per adsorbed molecule. But with the piston film technique, it is possible to investigate the film-forming properties by a direct

measurement of F_{ba} and γ_b; then using Eqs. (15) and (16) the value of the work of adhesion (W_{ba}) and the interfacial tension (γ_{ab}) of each hydrocarbon can be calculated. Therefore, the remainder of the research reported here was concerned with the application of the above theoretical relations and interpretations to the effect of unsaturation and isomerism on the spreading pressure, interfacial tension, and reversible work of adhesion of a variety of pure alkanes, alkenes, alkynes, and aromatics. Such an effort is timely, because ever since the pioneering work of Harkins and Feldman (7) and the much later work of Washburn and coworkers, especially that of Shewmaker, Vogler, and Washburn (6), hardly any data have been published on the initial spreading coefficient, spreading pressure, and reversible work of adhesion of organic compounds on liquid substrates.

EXPERIMENTAL MATERIALS AND TECHNIQUES

Measurement of Spreading Pressure

Spreading pressures of hydrocarbons on water were measured with a modified Cenco "hydrophil" film balance and an insoluble piston monolayer of pure eicosyl alcohol. The trough, which was made of 18/8 stainless steel, 69.0 cm long, 14.1 cm wide, and 1 cm deep, was heavily coated with a high-melting, white, paraffin wax. Film pressures were measured on a simple torsion balance fitted with either a 0.0070-in.-diameter piano steel wire or a 0.020-in.-diameter phosphorbronze torsion wire, depending on the sensitivity needed. End loops to prevent leakage of film past the float were thin ribbons of either Teflon or FEP Teflon. The floating barrier was made of a thin sheet of aluminum coated with a uniform 0.0005-in. layer of Dupont "Teflon Finish." A good reversible and rectilinear plot of torque vs angular twist was obtained on increasing and decreasing the load, thus proving that the torsion wire was free of hysteresis and slip over the torque range used.

Washburn and Keim (1) showed that the spreading pressures were the same for piston monolayers of stearic or palmitic acids or tristearin. We obtained the same results using eicosyl or octadecyl alcohol and preferred an alcohol because its film properties were not affected by the pH of the water or the presence of traces of polyvalent metallic ions. The essential requirements for the piston monolayer need to be clarified. Obviously, the piston film must not be able to evaporate or to dissolve to a measurable extent in the time required for the measurement of a spreading pressure or the duration of an experiment. The film pressure (F) vs area per molecule (A) for the piston film monolayer should be free from either a film collapse process or a film solidification stage over the film pressure range to be used in the experiments. Finally, the piston monolayer should have a low solubility in the liquid whose spreading pressure is measured. However, the solubility involved here is that of the oriented adsorbed film in the spreading drop of liquid lying <u>next</u> to it on the water. This might be called the lateral solubility because a two-dimensional step is involved in the contact of solute and solvent. In working with any new class of spreading liquids, it is desirable to try several piston films to be sure the results are independent of the choice of piston film material.

A piston film of pure eicosyl alcohol was used in these experiments; it was applied dropwise in pure benzene solution to the clean surface of the distilled water at a convenient central point between the fixed and the floating barriers. As the benzene evaporated from the dilute solution, the film pressure was slowly built up until it was high enough for convenient manipulation of the spreading liquid hydrocarbon samples.

Measurement of Surface Tension

Measurements of the surface tension of each hydrocarbon were made when necessary using the differential capillary-rise apparatus described by Fox and Chrisman (10)

and Ellison and Zisman (11). From the difference in height of the test liquid in the two parallel glass, precision-bore capillaries and the known capillary diameters the surface tension (γ_b) of the liquid could be computed. Determinations were made using a cell calibrated with known liquids by plotting a nearly rectilinear graph of ΔH vs k^2, where ΔH is the difference in height of the menisci in the two capillary tubes and k^2 is an instrument constant. This graph was then used to obtain k^2 for corresponding values of ΔH; to obtain the surface tension γ these quantities were used in the well-known capillary rise equation

$$\gamma = (1/2)\, k^2\, gD\, (\Delta H) \tag{17}$$

where D is the specific gravity of the liquid. This equation was valid because the capillaries were circular and small in diameter and the contact angle of each liquid with the glass was zero. The capillary-rise cell was cleaned prior to each determination by a 5-minute treatment with hot 50/50 concentrated nitric acid-sulfuric acid solution. This was followed by thoroughly washing it in distilled water and then baking it in a clean stainless steel oven for 2 hours at 110°C.

Experimental values of γ_b so obtained are given in Table 1. In many instances reliable literature values were available for the surface tensions of some of the hydrocarbons investigated, and these were used as indicated in Tables 2, 3, and 4.

Table 1
Summary of Surface Tension Measurements at 20°C

Compound*	ΔH (cm)	k^2 (cm^2)	D (g/cm^3)	γ_b (dynes/cm)
3-Methyl-1-pentene	10.348	0.0525†	0.670‡	17.27
2-Methyl-1-pentene	10.874	0.0553†	0.6820‡	18.50
cis-4-Methyl-2-pentene	10.352	0.0526†	0.672‡	17.32
trans-4-Methyl-2-pentene	10.323	0.05245†	0.670‡	17.23
4-Methyl-2-hexyne	11.170	0.05670†	0.7386§	20.92

*Compounds prepared at NBS for NACA aircraft fuel program.
†Values obtained from calibration graph of capillary rise cell.
‡Data from Ref. 12.
§Data from Ref. 13.

Sources and Purity of Hydrocarbons

The hydrocarbons used in this work were obtained from several sources and were the best materials available at the time; these are listed in Tables 2, 3, and 4 according to source and type. In Tables 2 and 4 are listed the aromatics and most of the paraffins studied. These were obtained from the National Bureau of Standards as American Petroleum Institute (API) "Standard Samples," from the Phillips Petroleum Company as "Research Grade Chemicals," and from the University of Wisconsin. The API and Phillips' materials were used in these experiments shortly after receipt.

In Table 3 are listed some specially prepared paraffins, olefins, and acetylenic hydrocarbons. These were made available in small quantities through the cooperation of the Engine Fuels Section of the National Bureau of Standards (NBS). Each compound was either synthesized or purified at NBS at part of an earlier investigation of aircraft-fuel components for the then National Advisory Committee for Aeronautics (NACA), the Army Air Force (later the Department of the Air Force), and the Department of the Navy,

Table 2
Alkanes—Spreading Pressures and Properties Derived Therefrom (All Data at 20°C)

Hydrocarbon and Source	B.P. (°C) (Ref. 12)	γ_b (dynes/cm) (Ref. 14)	F_{ba} (dynes/cm)	S_{ba} (dynes/cm)	γ_{ab} (dynes/cm)		W_{ba} (ergs/cm^2)
					Calculated	Measured	
n-Pentane*	36.1	15.98	5.90	6.6†	50.9	49.0 (17) 50.2 (15)	39.6 (17) 37.9
2-Methylbutane*	27.9	14.97	7.70	9.44 (7)	50.1	49.64 (18)	37.6 36.9 (18)
n-Hexane‡	68.7	18.42	3.70	3.37 (7) 3.41 (15)	50.7	50.8 (19) 51.25 (18) 50.80 (15)	40.5 40.54 (15) 39.98 (18)
2,2-Dimethylbutane‡	49.7	16.18	6.90	—	49.7	—	39.3
2,3-Dimethylbutane‡	58.0	17.43	5.60	—	49.8	—	40.5
2-Methylpentane‡	60.3	18.41	5.50	—	48.9	—	42.3
3-Methylpentane*	63.3	18.11	4.80	—	49.9	—	41.0
n-Heptane‡	98.4	20.26	1.80	1.3 (15)	50.7	51.2 (19) 52.55 (20) 51.23 (15) 50.2 (17)	42.3 41.83 (15) 42.95 (17)
3-Ethylpentane*	93.5	20.16	2.10	—	50.5	—	42.4
2,4-Dimethylpentane*	80.5	18.12	4.70	—	50.0	—	40.9
3-Methylhexane*	91.9	19.56	2.80	—	50.4	—	41.9
n-Octane*	125.7	21.80	0.10	0.22 (7) -0.62 (15)	50.9	51.7 (19) 50.8 (18) 51.68 (15)	43.7 42.81 (15) 43.76 (20)
3-Ethylhexane*	118.5	21.54	0.50	—	50.8	—	43.6
3-Methylheptane*	118.9	21.30	1.0	—	50.5	—	43.6
2-Methyl-3-ethylpentane*	115.7	21.54 (16)	1.1	—	50.2	—	44.2
2,2,4-Trimethylpentane*	99.2	18.85	3.90	4.4 (6)	50.0	50.1 (15)	41.6
n-Nonane*	150.8	22.92	<0	—		—	

*National Bureau of Standards "Standard Samples of Hydrocarbons."
†Calculated from Ref. 15 for γ_{ab} and Ref. 16 for γ_b.
‡Phillips Petroleum Co., "Research Grade Hydrocarbons."

Table 3
Alkanes and Alkenes—Spreading Pressures and Properties Derived Therefrom
(All Data at 20°C)

Hydrocarbon and Source*	B.P. (°C) (Ref. 12)	γ_b (dynes/cm)	F_{ba} (dynes/cm)	γ_{ab} Calc. by Eq. (16) (dynes/cm)	W_{ba} (ergs/cm^2)
2,2,3-Trimethylbutane	80.9	18.81 (14)	4.23	49.8	41.8
2,2-Dimethylpentane	79.2	18.03 (14)	5.14	49.6	41.2
2,3-Dimethylpentane	89.8	19.97 (14)	3.53	49.3	43.5
2,2,3-Trimethylpentane	109.8	20.69 (14)	2.10	50.0	43.5
2,3,4-Trimethylpentane	113.5	21.18 (14)	2.58	49.0	44.8
1-Octene	121.3	21.78 (14)	4.09	46.9	47.7
1-Heptene	93.6	20.24 (14)	6.32	46.2	46.8
1-Hexene	63.5	18.41 (14)	8.34	46.0	45.2
4-Methyl-1-pentene	53.9	17.97 (14)	10.22	44.6	46.2
3-Methyl-1-pentene	54.1	17.27	10.37	45.2	44.9
2-Methyl-1-pentene	60.7	18.50	11.04	43.3	48.0
cis-4-Methyl-2-pentene	56.3	17.32	10.20	45.3	44.8
trans-4-Methyl-2-pentene	58.6	17.22	10.00	45.6	44.4
2,2,4-Trimethyl-1-pentene	101.4		17.6†		
4-Methyl-2-hexyne	99.5	20.92	21.8‡	30.1	63.6
2,2,4-Trimethyl-2-pentene	104.5		35.0§		

*Compounds prepared at NBS for the NACA aircraft fuel program.
†After two percolations through activated alumina this value rose to 26.1.
‡Erratic behavior, spreading pressures gradually decreased to 20.0 dynes/cm.
§Before percolation through activated alumina. Two phases appeared in the filtrate after three percolations.

Bureau of Aeronautics (superseded by the Bureau of Weapons and later by the Naval Air Systems Command). The compound preparations and properties have been reported previously by the NBS investigators (13,23,24). Each compound is believed to be of very high purity, in most cases exceeding 99 mole-percent. Usually, the purity of each compound was determined by a freezing-point determination; however, in several cases the low-temperature calorimeter and/or the mass spectrometer was used for purity determination (25).

Yet even organic materials of such high isomeric purity have to be purified further for this type of study. The most troublesome contaminants in the test sample were believed to be peroxides, known to form readily in hydrocarbons upon standing in contact with atmospheric oxygen. Despite their low concentrations, these impurities had to be removed, because organic peroxides and their decomposition products are usually so surface-active that concentrations as low as 0.001 wt-% can cause marked spreading of the hydrocarbon drop on water. Dust particles and traces of organic vapor in the air also had to be eliminated because they could affect the determination of the spreading pressure.

Table 4
Aromatics—Spreading Pressures and Properties Derived Therefrom (All Data at 20°C)

Hydrocarbon and Source	B.P. (°C) (Ref. 12)	γ_b (dynes/cm) (Ref. 14)	F_{ba} (dynes/cm)	S_{ba} (dynes/cm)	γ_{ab} (dynes/cm) Calculated	γ_{ab} (dynes/cm) Measured	W_{ba} (ergs/cm^2)
Benzene*	80.1	28.88	9.8	9.9† (5,6) 9.8 (7)	34.1	35.0 (17) 33.9 (5) 39.2 (6) 34.0 (6) 35.1 (21) 34.96 (20)	66.6 (17) 67.6 66.74 (20)
Methylbenzene*	110.6	28.53	8.3	8.5† (5,6) 6.84 (1,7)	36.0	35.7 (5,6) 36.06 (18)	65.3
Ethylbenzene*	136.2	29.04 (22)	6.1	5.6 (7) 6.2† (6)	37.7	33.92 (19) 37.4 (6) 38.7 (18)	64.2 62.6 (18)
n-Propylbenzene*	159.2	28.99 (22)	4.2	5.1† (6)	39.6	38.5 (6) 35.24 (19)	62.2
n-Butylbenzene*	183.3	29.23 (22)	2.2	3.8† (6)	41.4	35.80 (19) 39.6 (6)	60.7
n-Hexylbenzene‡	226.1	30.14 (22)	<0				
1,3,5-Trimethylbenzene*	164.7	28.80 (22)	5.2	5.6 (7)	38.8		62.8
1,2-Dimethylbenzene*	144.4	30.00	5.6	6.85 (7)	37.2	36.06 (18)	65.6 66.6 (18)
1,3-Dimethylbenzene*	139.1	28.6	6.6	6.19 (7)	37.6	37.9 (18)	63.8 63.6 (18)
1,4-Dimethylbenzene*	138.4	28.33	6.7	6.70 (7)	37.8	37.8 (18)	63.4 63.4 (18)
1,3,5-Triethylbenzene‡	215.0		1.0				

*National Bureau of Standards "Standard Samples of Hydrocarbons."
†Data for 25°C.
‡University of Wisconsin.

Final purification of the saturated alkanes was relatively easy and was accomplished by slowly percolating each liquid through a small adsorption column packed with Florisil, fuller's earth, or activated silica gel. This method led to a lower and more reproducible value of the spreading pressure. The silica gel was a 28-200 mesh (Davison Grade 912).

As is well known, the unsaturated aliphatic hydrocarbons react quickly with atmospheric oxygen. Since some of the olefins and acetylenes investigated were believed contaminated with peroxides, various adsorbents were tried in attempts to purify them. Following are some of the results of these experiments:

1. Davison Grade 923 silica gel (100-200 mesh), a special, iron-free silica gel which does not polymerize olefins, was used first, since it appeared to be tailor-made for the treatment of unsaturates. However, in each case tried the inability of this absorbent to completely remove the peroxide was evidenced by the subsequent spreading behavior of the hydrocarbon sample. When added to the surface of the water, the hydrocarbon filtrate broke into smaller droplets, and extremely erratic and unreproducible values of the spreading pressure were obtained. Therefore, use of this adsorbent for treatment of peroxide-containing olefins and acetylenes was discontinued.

2. Alcoa Grade F-2 activated alumina adsorbent was also tried after being activated at 400°C for 4 hours in a stream of nitrogen. Use of this adsorbent on the unsaturated hydrocarbons led to the same erratic results obtained with silica gel. In one case, repeated percolation of 2,4,4-trimethyl-2-pentene resulted in increasingly higher values of the spreading pressure, until finally a second phase appeared in the filtrate. This was confirmatory evidence that the alumina was accelerating the decomposition of peroxides to more surface-active compounds, perhaps glycols. The use of this adsorbent on such compounds was discontinued.

3. Sealing in vacuo produced olefins of sufficient purity to yield reproducible and significant results. The procedure adopted consisted in sealing the freshly distilled hydrocarbon under its own vapor pressure (26) and in storing the sample cold and in the dark until used in these experiments. Since very little oxygen was present when this operation was performed properly, insufficient peroxides and concomitant polymers were present to interfere with the film measurements. Spreading experiments on olefinic materials sealed into glass in this manner resulted in the lowest spreading pressures and the most significant and reproducible results obtained; the acetylenic materials, unfortunately, had not been bottled immediately upon distillation and therefore did not yield such reproducible data.

Method of Calculating Values of γ_{ab} and W_{ba}

From Eq. (16) the value of the interfacial tension (γ_{ab}) was computed by using measured values of F_{ba} and γ_b. Since γ_a, the surface tension of pure water at 20°C, is 72.80 dynes/cm, Eq. (16) becomes

$$\gamma_{ab} = 72.80 - \gamma_b - F_{ba}. \tag{18}$$

The work of adhesion to water (W_{ba}) was computed by Eq. (15) using measured values of γ_b and F_{ba}.

Results so obtained for each of the hydrocarbons investigated are given in Tables 2, 3, and 4, in which are also listed the surface tension (γ_b), the observed initial spreading pressure (F_{ba}), the reported initial spreading coefficient (S_{ba}), the interfacial tension (γ_{ab}) as calculated by Eq. (16), the interfacial tension ($\gamma_{a'b'}$) reported in the literature, and the reversible work of adhesion to water (W_{ba}) as calculated by Eq. (15).

GENERAL DISCUSSION AND CONCLUSIONS

Plotting the initial spreading pressure (F_{ba}) of each homologous series of hydrocarbons reported in Tables 2, 3, and 4 against the boiling point (Fig. 1) resulted in several nearly parallel straight lines with negative slopes, each of which corresponded to an homologous series. Similarly, plotting F_{ba} against N (the number of carbon atoms per molecule), for the n-alkane and 1-alkene series, resulted in straight lines of negative slope (Fig. 2). A number of interesting conclusions may be drawn from these figures. It can be seen (Fig. 2) that the first n-alkane to have a negative initial spreading pressure is n-nonane. By extrapolation of the 1-alkene line the first member of this series predicted to be essentially nonspreading would be 1-decene.

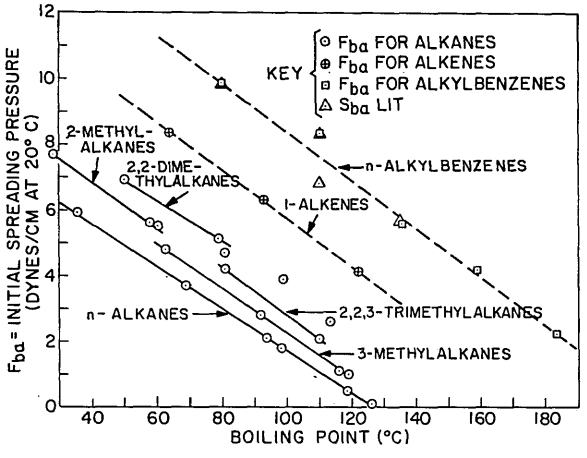

Fig. 1 - Initial spreading pressures as functions of boiling points

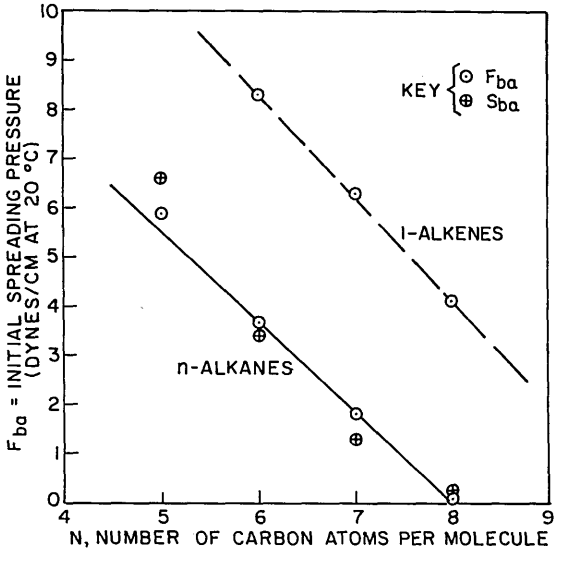

Fig. 2 - Initial spreading pressures as functions of the numbers of carbon atoms

It is seen from either figure that the 1-alkene line is displaced from the n-alkane line on the ordinate axis by approximately 4.2 dynes/cm. This displacement, which could have been caused only by the contribution of the double bond, is good experimental evidence of the hydrophilic nature of the olefinic bond (—CH=CH—). Furthermore, on comparing the value of F_{ba} for 3-methylhexane in Table 2 with that for the acetylene, 4-methyl-2-hexyne in Table 3, it is seen that the acetylene has a spreading pressure about 19 dynes/cm greater. This large difference in spreading pressure results from the introduction of the acetylenic grouping (—C≡C—). Since the acetylene compound was not as pure as most of the others investigated, the value of 19 dynes/cm is a rough approximation of the hydrophilic contribution by the triple bond.

Of interest is that the n-alkylbenzene family lies on the uppermost straight line of Fig. 1, for it proves that the unsaturated bonds in the benzene ring make benzene much more hydrophilic than either 1-hexene or n-hexane. However, the separation of the n-alkylbenzene and n-alkane lines is approximately 6.8 dynes/cm and not three times greater than the 4.2-dyne/cm separation of the 1-alkene and n-alkane lines. Thus we have evidence that the three aromatic double bonds usually assigned to the benzene ring are each less hydrophilic than one olefin bond.

When a plot of F_{ba} versus boiling point is made for members of the homologous series of n-alkanes, for the series comprising 3-methylpentane, 3-methylhexane, and 3-methylheptane, and for the series 2,2-dimethylbutane and 2,2-dimethylpentane, three straight parallel lines result. Although not labeled, the point for 2,2-dimethylhexane can be identified with confidence from the geometry of Fig. 3.

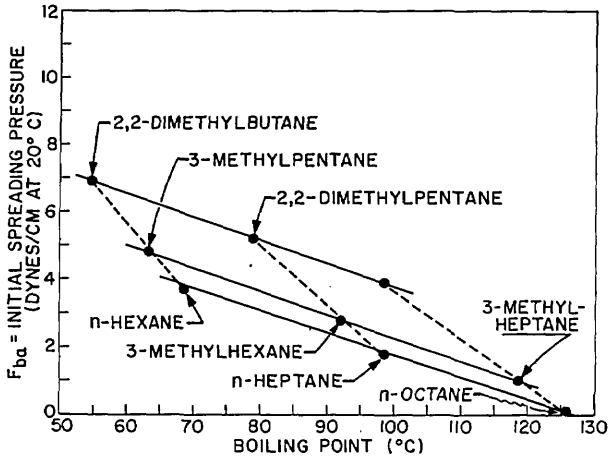

Fig. 3 - Effect of homology on the initial spreading pressures as functions of boiling points

From Table 3 it is evident that cis-4-methyl-2-pentene has a slightly higher value of F_{ba} (and of W_{ba}) than trans-4-methyl-2-pentene. Therefore, the cis configuration is more hydrophilic than the trans. This is expected, since the cis configuration is known to be more flexible and thus less sterically hindered than the trans and therefore will permit easier access of the double bond to the water surface.

As S_{ba} was computed from Eq. (1), it involves the three surface tensions, γ_b, γ_a, and γ_{ab}, and hence is sensitive to errors in γ_{ab} arising from hydrophilic impurities. Evidently the four literature values of S_{ba} for alkylbenzenes are in good to fair

agreement with the upper graph of Fig. 1. Figure 2, which is a graph of F_{ba} vs N, the number of carbon atoms in the aliphatic chain, shows that the straight line for the n-alkanes is parallel and below that for the 1-alkenes and also that the literature values of S_{ba} for the n-alkanes are in good to fair agreement with the lower straight line graph of F_{ba} vs N.

Values of γ_{ab} calculated from Eq. (16) have been compared in Tables 2 and 4 with the best literature values. In general, the literature values were obtained experimentally after allowing the hydrocarbon liquid and the water in contact with it to become mutually saturated at that temperature; hence, each value cited is $\gamma_{a'b'}$ and not γ_{ab}. Therefore, differences may appear between experimental values of the interfacial tension and our calculated γ_{ab}. We cannot state any generalities at present about the magnitudes of these differences. Certainly, they will vary with the solubility of b and a. Despite this problem, the calculated values of γ_{ab} for the hydrocarbons investigated were generally in good agreement with the experimental values of $\gamma_{a'b'}$. In Fig. 4 the calculated values of γ_{ab} and the observed values of $\gamma_{a'b'}$ are plotted against the boiling points. The difficulties in judging the most reliable literature values of $\gamma_{a'b'}$ are evident from the scatter of these data when plotted for the n-alkanes and the alkyl benzenes in Fig. 4. There is excessive spread of some literature values for ethylbenzene, n-propylbenzene, and n-butylbenzene. In general, values of $\gamma_{a'b'}$ for the high-boiling hydrocarbons are still less reliable than those of the lower boiling compounds. Despite these problems, it is evident from Fig. 4 that the interfacial tensions clearly distinguish between the alkanes, alkenes, and alkyl benzenes and reveal a marked decrease with increased attraction for water.

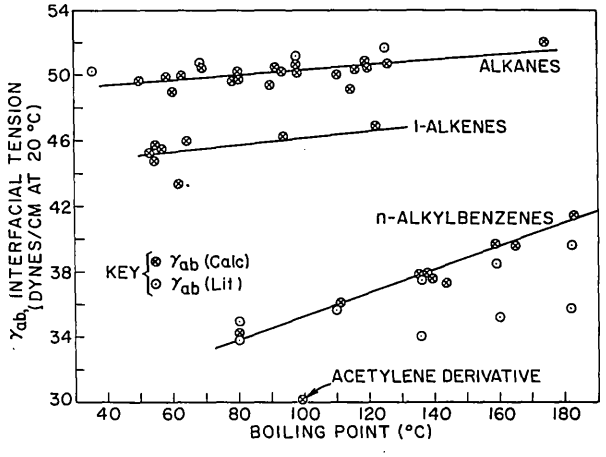

Fig. 4 - Comparison of the calculated values of γ_{ab} and observed (literature) values of γ_{ab} (actually $\gamma_{a'b'}$) as functions of boiling points for all hydrocarbons investigated

Antonoff's rule (27-30) that the interfacial tension can be calculated from the surface tension difference between the liquids has been much discussed. It appears to be agreed by Antonoff and many other investigators (31,32) that the rule is correct only when applied to each liquid saturated with the other, i.e., when

$$\gamma_{a'b'} = \gamma_{a'} - \gamma_{b'} . \tag{19}$$

Nevertheless, it is interesting to compare the values of γ_{ab} calculated here with $\gamma_a - \gamma_b$. The results, given in Table 5, show that $\gamma_a - \gamma_b$ is usually too large and is only a good approximation for n-octane. As for n-butylbenzene, the value of $\gamma_a - \gamma_b$ is much too large. Here the effect of neglecting the difference in γ_{ab} and $\gamma_{a'b'}$ probably becomes more important because of the greater solubility of water in aromatics than in aliphatic hydrocarbons.

Table 5
Comparison of γ_{ab} with Values Calculated by $\gamma_{ab} = \gamma_a - \gamma_b$
(All Data at 20°C)

Liquid	γ_{ab} Calc. by Eq. (16) (dynes/cm)	$\gamma_a - \gamma_b$ (dynes/cm)	γ_{ab} (Lit.) (dynes/cm)	Ref.
n-Pentane	50.9	56.82	50.2	15
n-Hexane	50.7	54.38	50.8	19
n-Heptane	50.7	52.54	51.2	19
n-Octane	50.9	51.00	51.7	19
2,2,4-Trimethylpentane	50.0	53.95	50.1	15
Benzene	34.1	43.92	35.1 34.0	21 5
n-Butylbenzene	41.4	43.57	39.6	6

Figures 5 and 6 are plots of W_{ba} for each of the indicated hydrocarbons against the normal boiling point and N, respectively. For comparison, graphical points are shown of the values of W_{ba} calculated by the Dupré equation (Eq. (12)) using measured values of γ_a, γ_b, and $\gamma_{a'b'}$. Here again we have neglected the difference between γ_{ab} and $\gamma_{a'b'}$. Values of W_{ba} for the alkane and alkene series increase with increasing boiling point (or N). The nearly constant displacement in Fig. 5 of approximately 5 ergs/cm^2 between the paraffin and olefin series arises from the adhesional energy caused by the hydrophilic nature of the aliphatic double bond.

More significant in molecular terms is ω_{ba}, the reversible work of adhesion per adsorbed mole of hydrocarbon. This can be calculated by the evident relation

$$\omega_{ba} = \frac{W_{ba}\ \sigma_b\ (6.02\times10^{23})}{4.18\times10^7}\ \text{cal/g-mole} \tag{20}$$

where σ_b is the area occupied at the organic liquid/water interface by each molecule of hydrocarbon. There is much surface-chemical evidence in the more recent literature which confirms de Boer's generalization (33) that if the molecular chain is not too long, the molecule lies as flat as is sterically possible in order to get the greatest number of most polarizable atoms in the surface and so minimize the surface energy. Measurements on Stuart-Briegleb molecular ball models resulted in the values of σ_b assigned in the second column of Table 6 for the hydrocarbons of interest. In the third column are values of W_{ba} taken from Tables 2, 3, and 4, and in the fourth column are the values of ω_{ba} calculated in accordance with Eq. (20).

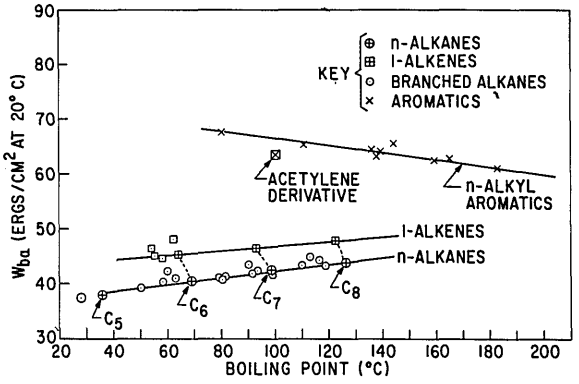

Fig. 5 - Values of W_{ba} as functions of boiling points for all hydrocarbons investigated

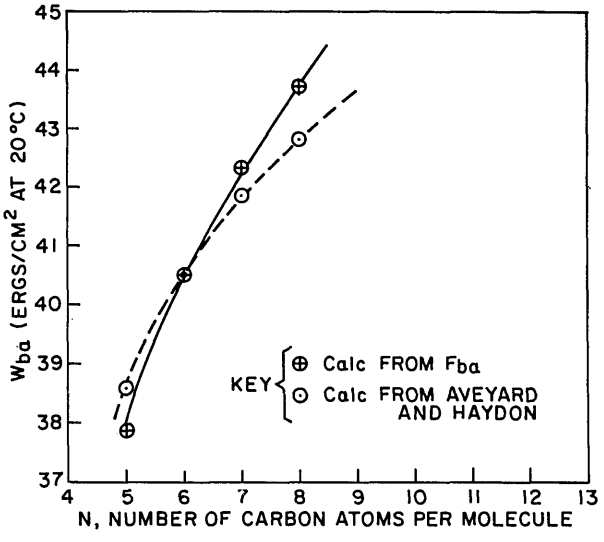

Fig. 6 - Values of W_{ba} as functions of the numbers of carbon atoms for n-alkanes

A plot (not shown) of ω_{ba} vs the number of carbon atoms per molecule (N) is a good straight line for the n-alkane series, and from it the reversible work of adhesion per methylene group was found to be 395 cal/g-mole. Using the 1-alkene series the value obtained by the difference in ω_{ba} between 1-octene and 1-hexene was 425 cal/g-mole of methylene groups; however, a larger series of 1-alkenes is desirable for a more reliable calculation. In addition, the problems of maintaining high enough purity are more difficult with the alkenes than the alkanes. Therefore, the value calculated from the n-alkane series is considered more reliable. A plot of ω_{ba} vs N for the n-alkylbenzenes shows more departure from a good straight line. However, the data for the series ethylbenzene, n-propylbenzene, and n-butylbenzene plot as a straight line from which the value of 400 cal/g-mole is calculated for the methylene group. By assigning the value of 400 cal/g-mole to the methylene group, one can calculate from the value of ω_{ba} = 3270 cal/g-mole for n-octane the value ω_{ba} = 435 cal/g-mole for methyl end

Table 6
Calculation of Reversible Work of Adhesion Per Gram Mole
(All Data Relate to 20°C)

Liquid	σ_b* (Å^2)	W_{ba} (ergs/cm^2)	ω_{ba} (cal/g-mole)
n-Pentane	37	37.9	2070
n-Hexane	42	40.5	2450
n-Heptane	47	42.3	2870
n-Octane	52	43.7	3270
1-Hexene	40	45.2	2590
1-Heptene	45	46.8	3030
1-Octene	50	47.7	3440
Benzene	34	67.6	3310
Methylbenzene	39.4	65.3	3700
Ethylbenzene	46	64.2	4250
n-Propylbenzene	51	62.2	4570
n-Butylbenzene	56	60.7	4950
Cyclohexane	31.5	46.7†	2130

*Measured from Stuart-Briegleb models of molecules in extended configuration with all C—C bonds in the plane of measurement.
†Calculated from the Dupré equation using γ_a = 72.80, γ_b = 24.95, and γ_{ab} = 51.0 from Ref. 34.

groups. But this value is subject to the qualification that the flatwise adsorption of the n-alkanes on the water surface causes the effect of the methyl terminal groups on ω_{ba} to be different, and probably greater, than that which would be found if the n-alkane were adsorbed with the principal axis at right angles to the water surface. It is interesting that the value of 400 cal/g-mole of methylene groups was reported by Bigelow, Glass, and Zisman (35) many years ago from the study of the effect of temperature on the oleophobic (or retractive) properties of the family of pure primary n-alkyl amines on platinum; furthermore, Jones and Ottewill (36) obtained 420 cal/g-mole for the free energy change on adsorption per $-CH_2-$ group from their more recent investigation of the vapor adsorption of the pure hydrocarbons on water between 0° and 15°C.

The value which must be assigned to ω_{ba} for a terminal double bond can be calculated by the difference in values of ω_{ba} for 1-octene and n-octane or 3440 - 3270 = 170 cal/g-mole. We can also calculate the adhesional work per gram mole of terminal olefinic ($CH_2{=}CH-$) groups from ω_{ba} for 1-octene as follows: 1-octene comprises one CH_3- group, five $-CH_2-$ groups, and one terminal $CH_2{=}CH-$ group. Using 435 cal/g-mole for the value of ω_{ba} for the methyl terminal, 395 cal/g-mole for each methylene group, and 3440 cal/g-mole for 1-octene gives the value 1030 cal/g-mole for the terminal olefinic group ($CH_2{=}CH-$).

By comparing the value of ω_{ba} for benzene with that for cyclohexane an estimate can be made of the adhesional work per unsaturated aromatic —CH=CH— group. From Rose and Seyer's data (34) for cyclohexane at 20°C we obtained the value W_{ba} = 46.7 ergs/cm^2, since γ_b = 24.95 and γ_{ab} = 51.0 dynes/cm. Measurements on a Stuart-Briegleb molecular ball model of cyclohexane revealed that σ_b = 31.5 Å^2, regardless of whether the molecular model was arranged in the "chair" or "boat" form. Hence, for cyclohexane ω_{ba} = 2130 cal/g-mole. The difference between ω_{ba} for benzene and cyclohexane is 3310 - 2130 = 1180 cal/g-mole. However, this difference is for three pairs of aromatic carbon-carbon bonds. Therefore, one obtains 393 cal/g-mole for each pair of aromatic double bonds comprising the group —C=C—. This value is only about one-third that for the terminal olefinic group (CH_2=CH—). For lack of data on ω_{ba} for other isomers of the olefin family, we cannot compute the contribution of the nonterminal —CH=CH— group and compare that with its aromatic analogue.

Recent investigations by our laboratory on the surface-chemical displacement of water (37) and of organic liquids (38,39) from solid surfaces have revealed that the most effective liquid-displacing agents should have high equilibrium spreading pressures, low surface tensions, and some solubility in the liquid to be displaced. These requirements led to the need for more data on S_{ba} for other promising liquid compounds and to our use of the piston monolayer method for measuring it. It now appears timely to obtain in the same way the values of S_{ba}, γ_{ab}, and W_{ba} for the lower fluorocarbons, silicones, and various other compounds.

Much more information is needed on the effect of molecular structure on γ_{ab}, W_{ba}, and ω_{ba} because of their fundamental value in research aimed to explain the effect of surface constitution on adhesion. A further investigation is needed of the experimental conditions under which the piston film method gives values of $F_{b'a}$ rather than F_{ba} or $F_{b'a'}$. To this end an investigation of the homologous family of the n-alkanols will be reported later.

As Ellison and Zisman (4) and Jarvis and Zisman (40) have already shown, the piston monolayer method coupled with a suitable choice of the piston monolayer material is an excellent method for measuring these quantities on nonaqueous liquid substrates. Further work in this direction is in progress.

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13. ABSTRACT

An investigation has been made on the effect of molecular structure and unsaturation upon the initial spreading pressure (F_{ba}) on water of numerous representative low-boiling hydrocarbons of exceptional purity. These compounds included members of the paraffin, olefin, aromatic, and acetylene families. Measurements of F_{ba} were made at 20°C using the "piston monolayer" method. In agreement with the results of Washburn et al., F_{ba} was always equal (or nearly so) to the initial spreading coefficient (S_{ba}).

The relations between the initial, semi-initial, final, and equilibrium spreading pressures and the corresponding spreading coefficients are discussed. The conditions under which the initial spreading pressure (F_{ba}) is equal to the Harkins initial spreading coefficient (S_{ba}) is established thermodynamically. It is shown that the value of S_{ba} and the initial value of γ_{ab}, the interfacial tension against water, and W_{ba}, the initial value of the reversible work of adhesion, can be calculated from F_{ba}, the surface tension of the organic liquid (γ_b), and the surface tension of water (γ_a).

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Alkanes						
Alkenes						
Organic compounds						
Adhesion						
Surface tension						
Hydrogen bonding						
Thermodynamics						
Structure of water						
Molecular structure						

When F_{ba} was plotted against the normal boiling point for several series of homologous compounds, a series of straight and nearly parallel lines of negative slope were obtained. The amount by which the lines for the different homologous series were displaced from each other was a measure of the differences in hydrophilicness. Therefore, the results are used to show the relation of the effect of branching and unsaturation on γ_{ab} and W_{ba}. Finally, additional data on the hydrophilic nature of olefinic, aromatic, and acetylenic bonds are presented and discussed in terms of the molar work of adhesion (ω_{ba}).