

The Relation of Initial Spreading Pressure of Polar Compounds on Water to Interfacial Tension, Work of Adhesion, and Solubility

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ABSTRACT

An investigation has been made of the effect of chain length and solubility upon the spreading on water of the homologous series of pure normal alcohols from 1-butanol to 1-decanol. Spreading pressures were measured at 20°C using the piston-monolayer method. Each measured value corresponded to the semi-initial spreading pressure, which was equal, within experimental error, to the initial spreading pressure. Surface tensions of these alcohols were measured, as were the interfacial tensions with water. It is concluded that the spreading pressure of each alcohol, together with its surface tension, can be used to calculate reliably the interfacial tension and the reversible work of adhesion to water.

Data for the spreading pressures on water of a variety of organic liquids are also given. With these data and literature values of the liquid surface tensions, calculations were made of the interfacial tensions and work of adhesion by means of the equations published by Pomerantz, Clinton, and Zisman. The calculated interfacial tension was plotted as a function of the best available literature value of the solubility of water in each organic liquid. Our results agreed well with Donahue and Bartell's logarithmic relationship between the interfacial tension and the degree of miscibility. A relationship is given from which solubility can be estimated from interfacial tension. Finally, the relation between the molar work of adhesion to water and the constitution of the adsorbed organic molecules is discussed.

PROBLEM STATUS

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

AUTHORIZATION

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THE RELATION OF INITIAL SPREADING PRESSURE OF POLAR
COMPOUNDS ON WATER TO INTERFACIAL TENSION, WORK OF
ADHESION, AND SOLUBILITY

INTRODUCTION

Harkins and Feldman (1) have described three stages of spreading of one liquid over another in terms of three spreading coefficients. The initial spreading coefficient S_{ba} referred to the spreading of pure liquid b over the clean surface of liquid a , the semi-initial spreading coefficient $S_{b'a}$ referred to the spreading of liquid b saturated with a over a clean surface of liquid a , and the final spreading coefficient $S_{b'a'}$ referred to the spreading of liquid b over the surface of liquid a after each liquid was saturated with the other. These three quantities were derived thermodynamically and were related to the surface and interfacial tensions γ_a , γ_b , and γ_{ba} as follows:

$$S_{ba} = \gamma_a - (\gamma_b + \gamma_{ba}), \quad (1)$$

$$S_{b'a} = \gamma_a - (\gamma_{b'a} + \gamma_{ba}), \quad (2)$$

and

$$S_{b'a'} = \gamma_{a'} - (\gamma_{b'a'} + \gamma_{ba'}), \quad (3)$$

where the superscript indicates the saturation of that liquid with the other.

Washburn and Keim (2) reported years ago the utility of the piston-monolayer method for the rapid, convenient determination of the spreading pressure of a drop of any spontaneously spreading organic liquid on water. Washburn and coworkers (3,4) later reported the spreading pressures of a number of organic compounds on water and pointed out that these values were either equal or nearly equal to the initial spreading coefficient S_{ba} of Harkins. Recently, Pomerantz, Clinton, and Zisman (5), using the piston-monolayer method, reported the spreading pressures of many other pure hydrocarbons on water and made the same general observation. They concluded that, because of the rapidity of the piston-monolayer method and the low mutual solubility of water and each of the hydrocarbons, their measurements yielded what they termed the initial spreading pressure F_{ba} . They also used the concept of a semi-initial spreading pressure $F_{b'a}$ and a final spreading pressure $F_{b'a'}$. More importantly, however, they presented a thermodynamic argument to demonstrate that F_{ba} is equal to S_{ba} , $F_{b'a}$ is equal to $S_{b'a}$, and $F_{b'a'}$ is equal to $S_{b'a'}$. It was then possible to rewrite Eqs. (1), (2), (3) as follows:

$$F_{ba} = S_{ba} = \gamma_a - (\gamma_b + \gamma_{ba}), \quad (4)$$

$$F_{b'a} = S_{b'a} = \gamma_a - (\gamma_{b'a} + \gamma_{ba}), \quad (5)$$

and

$$F_{b'a'} = S_{b'a'} = \gamma_{a'} - (\gamma_{b'a'} + \gamma_{ba'}). \quad (6)$$

Equation (4) was rearranged to obtain

$$\gamma_{ba} = (\gamma_a - \gamma_b) - F_{ba}. \quad (7)$$

Since the reversible work of adhesion W_{ba} between two liquid phases is given by the Dupré equation,

$$W_{ba} = \gamma_a + \gamma_b - \gamma_{ba}, \quad (8)$$

they combined Eqs. (7) and (8) to obtain the relation

$$W_{ba} = 2\gamma_b + F_{ba}. \quad (9)$$

The potential usefulness of the spreading-pressure measurement is made obvious by Eqs. (7) and (9). Although reliable measurements of γ_a and γ_b are made readily, the measurement of γ_{ba} has always been difficult because of its extreme sensitivity to surface-active impurities. The measurement of $\gamma_{b'a'}$ is even more difficult because of the long time usually needed for mutual saturation of liquids a and b . In contrast, the measurement of the spreading pressure of a liquid is rapid and convenient, and values of γ_{ba} and W_{ba} can be calculated from it when γ_a and γ_b are known.

Pomerantz, Clinton, and Zisman (5) have pointed out that if the spreading-pressure measurement is made slowly or if diffusion across the interface between the two liquids occurs rapidly, $F_{b'a}$ and $F_{b'a'}$ can be measured. In such circumstances, equations analogous to (7) and (9), containing semi-initial or final quantities, would be applicable. In systems where mutual solubility between the two liquid phases is slight, F_{ba} would be expected to be equal, or very nearly equal, to $F_{b'a}$. However, the questions still remain unanswered as to what quantity would be measured if there were significant solubility between the two liquid phases and whether Eqs. (7) and (9) would still be useful in calculating γ_{ba} and W_{ba} .

In an attempt to answer these questions, we have investigated the spreading pressures of the homologous series of pure normal alcohols from 1-butanol through 1-decanol using the piston-monolayer method and a water substrate. Because we found that sufficiently reliable literature values for the surface tensions of these homologous alcohols and their interfacial tensions with water were not available, we measured these quantities as well. Finally, we have considered the spreading properties of a variety of surface-active, organic liquids in addition to the n-alcohols.

EXPERIMENTAL METHODS AND MATERIALS

Spreading pressures were measured by placing a small drop of the alcohol under investigation on the water surface, where an insoluble piston monolayer had previously been spread. As the liquid drop spread, the pressure it created was transmitted through the piston monolayer to the floating barrier of a Langmuir-Adam-type film balance. By adjusting the floating and movable barriers, the liquid drop, which had now spread to a thin lens, could be forced to expand and contract slowly without altering the observed film pressure. This observed, constant film pressure is defined as the spreading pressure F_{ba} of the liquid alcohol.

The film balance was constructed of Pyrex and included a Cenco torsion head equipped with a paraffined-mica floating barrier and flexible polyethylene end loops (6). The torsion wire had a sensitivity of 3.38 degrees/dyne/cm. A more sensitive torsion wire could not be used, because the high spreading pressures encountered could have twisted it beyond the elastic limit. The precision of the spreading-pressure measurements reported here was ± 0.1 dyne/cm. The piston monolayer used was 11-(perfluorodecyl)-undecanoic acid and was spread on the water substrate from dilute n-hexane solution. The substrate water and the water used in interfacial-tension measurements were doubly distilled from Pyrex and, after equilibrating with the air, had a pH of 5.8. This piston monolayer was chosen because Bennett and Zisman (6) had found it stable at pH 5.8 and resistant to collapse at film pressures greater than 50 dynes/cm.

All surface-tension measurements reported here were made using the differential capillary-rise method of Sugden (7). We used the apparatus designed by Fox and Chrisman (8), which consisted of two parallel, precision-bore, glass capillaries having internal diameters of 0.10 and 0.05 cm. The difference in height of capillary rise of each

liquid was measured using a cathetometer with a precision of $\pm 3 \times 10^{-4}$ cm. From the measured difference in capillary rise, the density of the organic liquid, and the capillary diameters, the surface tension was calculated from the capillary-rise equation

$$\gamma = \frac{1}{2} \frac{H}{(1/b_1 - 1/b_2)} g(D-d). \quad (10)$$

The quantities b_1 and b_2 are the radii of curvature of the menisci, which were related to the capillary radii by using Sugden's tables (7). The reproducibility of surface-tension measurements was ± 0.05 dyne/cm. All spreading-pressure and surface-tension data were obtained at $20.0 \pm 0.1^\circ\text{C}$, and each value reported here represents the average of at least five independent determinations.

The alcohols were obtained from Lachat Chemicals, Inc., Chicago, Illinois; each had been checked for purity chromatographically and was reported to be of 99.5-wt-% purity by the manufacturer. Immediately prior to use, each alcohol was percolated slowly through a long, narrow column packed with activated adsorption alumina.

RESULTS AND DISCUSSION

Spreading Pressure, Surface Tension, and Work of Adhesion

To determine whether the initial $F_{b,a}$, semi-initial $F_{b',a}$, or final $F_{b'',a}$ spreading pressure was being measured, measurements on each alcohol were carried out in three different ways. One way involved measuring the spreading pressure of each alcohol as rapidly as practicable (about 30 sec), possibly before any diffusion of one liquid into the other had occurred, to obtain a "primary" value which might approximate $F_{b,a}$. These results are listed in the second column of Table 1. Another way involved rapidly measuring the spreading pressure of each alcohol after it had first been saturated with water, to approximate a value of $F_{b',a}$. Finally, a drop of pure alcohol, after the primary value

Table 1
Spreading Pressure, Surface Tension, Interfacial Tension,
and Work of Adhesion for n-Alcohol-Water Systems at 20°C

Alcohol	$F_{b,a}$ (dynes/cm)	γ_b (dynes/cm)	$\gamma_{b,a}$ (dynes/cm)		$\gamma_{b',a}$ (Literature) (dynes/cm)	$W_{b,a}$ (ergs/cm ²)
			Measured	Calculated		
1-Propanol	49.0*	23.6 [†]	0.00	0.15	—	96.2
1-Butanol	44.8	24.27	2.84	3.68	1.9 ²⁵ ° [‡]	93.34
1-Pentanol	42.5	24.90	5.33	5.35	4.4 ²⁵ ° [‡]	92.30
1-Hexanol	38.1	25.66	8.94	8.99	6.8 ²⁵ ° [‡]	89.42
1-Heptanol	36.9	26.09	9.78	9.76	7.95 [§] 7.7 ²⁵ ° [‡]	88.28
1-Octanol	35.3	26.89	10.27	10.56	8.52 [§]	89.08
1-Nonanol	34.7	27.65	10.31	10.40	—	90.00
1-Decanol	34.1	28.25	10.33	10.40	—	90.60

*Calculated from Eq. (4). [†]Extrapolated from Fig. 2. [‡]From Ref. 14. [§]From Ref. 12.

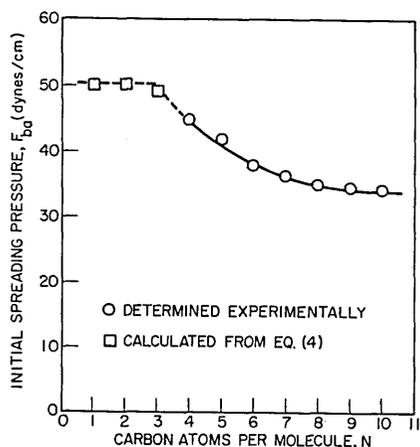


Fig. 1 - Initial spreading pressures of normal alcohols on water at 20°C

had been obtained, was allowed to remain on the water substrate for as long as possible while its spreading pressure was periodically measured to determine the extent to which the mutual solubilities of the two liquids would affect the measured pressures.

The primary spreading pressures obtained for the homologous series of alcohols are plotted as a function of N , the number of carbon atoms per molecule, in Fig. 1. It is seen that F_{ba} increased slowly with decreasing N in a nearly linear manner for the four highest liquid homologs, and then it increased more rapidly with further decrease in N . Because of the complete miscibility of 1-propanol, ethanol, and methanol in water, their spreading pressures could not be measured in this way. However, each of these alcohols must exert an initial spreading pressure, even if only briefly. Baker and Zisman (9) had pointed out that these spreading pressures could be calculated from Eq.

(4) when use was made of Pound's rule (10), which states that the interfacial tensions of these liquids must vanish because of their high solubilities in water. Thus, Eq. (4) reduces to $F_{ba} = \gamma_a - \gamma_b$. Using $\gamma_a = 72.75$ dynes/cm (11) for water and $\gamma_b = 23.70$, 22.77, and 22.55 dynes/cm, respectively, for 1-propanol, ethanol, and methanol (12), the calculated values of F_{ba} are 49.05, 50.48, and 50.20 dynes/cm. When these values are plotted as the dashed portion of Fig. 1, it is seen that the spreading-pressure curve approaches a limiting, horizontal asymptote for low values of N .

When the spreading pressures of the alcohols which had been saturated with water were measured and compared with those of the dry alcohols, identical results were obtained. Therefore, either the effect on the primary spreading pressure caused by the solubility of water in the alcohols was so slight that it did not affect the spreading-pressure measurement (i.e., $F_{ba} = F_{b'a}$) or else the diffusion of water from the substrate into the alcohol drop occurred so rapidly that it was impossible to measure F_{ba} . We do not believe the latter to be correct because of the speed possible in taking spreading-pressure measurements.

Two effects were observed when the spreading pressure was measured periodically on a drop of alcohol over a longer time. No change in the spreading pressure of 1-nonanol and 1-decanol was observed for times as long as 35 min. Reliable measurements could not be made over a longer time because of the gradual collapse of the piston monolayer, the slow film leakage past the floating barrier, or the evaporation of the more volatile alcohols. However, the spreading pressures of 1-octanol, 1-heptanol, and 1-hexanol decreased from the measured primary value by about 1.5 dynes/cm during a total elapsed time of 35 min. We presume that about the same effect would have been observed for 1-pentanol and 1-butanol had not evaporation of these compounds been so rapid as to preclude such a long series of measurements. This evidence indicates that there was so little mutual solubility between water and the longer chain alcohols ($N > 8$) that F_{ba} was being measured. But because of the slow dissolution of the shorter chain alcohols ($N \leq 8$) into the water substrate, the spreading pressures of these liquids decreased perceptibly in 35 min and were approaching the final spreading coefficient $F_{b'a}$. To further verify this conclusion, a second drop of dry alcohol was added to the substrate from which the original drop had evaporated. For each such alcohol, the spreading pressure of the second drop was precisely the decreased value that it had been for the original drop after 35 min (just before it had evaporated) rather than the value that it had been when first placed on the substrate. This means that the observed changes over a 35-min period were caused by changes in the substrate.

Thus, we can conclude that all primary spreading pressures reported here are either the initial F_{ba} or the semi-initial $F_{b'a}$ spreading pressures and that within the accuracy of our measurements they are equal (i.e., $F_{ba} = F_{b'a}$); in addition, the slowly decreasing spreading pressures observed over a longer period of time are approaching equilibrium and the final spreading coefficient $F_{b'a'}$.

The measured surface tension (in vapor-saturated air) of each member of the homologous series of n-alcohols is listed as γ_b in the third column of Table 1. These results, plotted in Fig. 2, are a linear function of N . Also shown in Fig. 2 are some of the more reliable surface-tension values given in the literature (12-15). Because of the purity of our alcohols, the accuracy of the method of Fox and Chrisman (8), and the self-consistency of our data, we believe our measured surface-tension values to be the most reliable yet reported; hence, we have used them in the calculations that follow.

It was impossible to measure the interfacial surface tensions as rapidly as the spreading pressures, because the capillary apparatus required that at least 15 min elapse before successive, reproducible readings could be obtained. Our measurements on the higher alcohols ($N > 8$) may represent the semi-initial values $\gamma_{b'a}$ and appear to be equal to the initial values γ_{ba} . For each of the lower alcohols ($N \leq 8$) the semi-initial value $\gamma_{b'a}$ was probably measured. The measured interfacial tensions between these alcohols and water are plotted in Fig. 3 as a function of N . The resulting curve appears to have a horizontal asymptote for $N > 10$. A straight line drawn for $N \leq 6$ resulted in a smooth extrapolation to $\gamma_{ba} = 0$ at $N = 3$, as shown by the dashed portion of the curve.

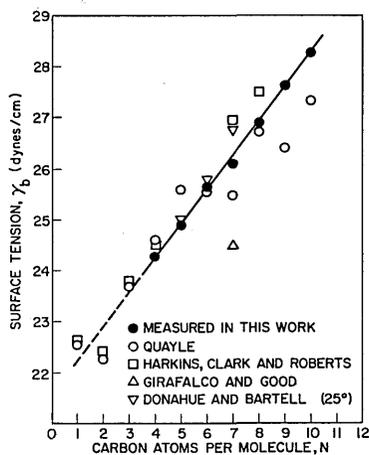


Fig. 2 - Surface tensions of normal alcohols at 20°C

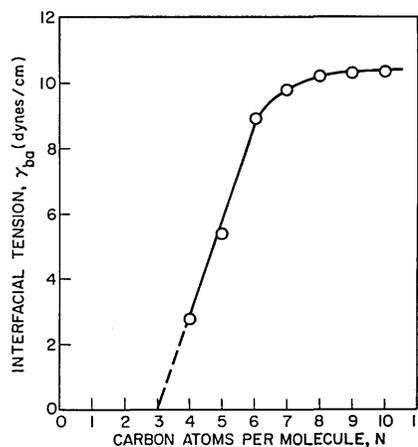


Fig. 3 - Measured interfacial tensions between normal alcohols and water at 20°C

We can now insert the measured initial spreading pressures and surface tensions of these alcohols, together with the known surface tension of water (72.75 dynes/cm at 20°C), into Eq. (7) and calculate the initial interfacial tensions of each alcohol-water system. Calculated results are given in the fifth column of Table 1 and can be compared with the measured values in the fourth column. The sixth column lists the most reliable and comparable literature values. In general, the agreement between the calculated and measured values of γ_{ba} is very good, for with the exception of 1-butanol, the calculated and measured values agree within 0.3 dyne/cm; in many cases the agreement is within the experimental error of the spreading-pressure measurement. In contrast, the literature values are from 1 to 2 dynes/cm smaller. This result is not surprising, since the calculated interfacial tension, having been based on the initial spreading pressure, was

necessarily the initial value γ_{ba} . The interfacial tensions cited in the sixth column of Table 1 are for systems at equilibrium and thus represent the final value γ_{ba}' . Although it is probably impossible to measure accurately the initial interfacial tension when there is high mutual solubility of the two liquids, the good agreement found here between calculated and measured values demonstrates the usefulness of primary spreading-pressure measurements in obtaining values of the interfacial surface tensions.

The seventh column of Table 1 lists the values obtained for the reversible work of adhesion W_{ba} between the various alcohols and water. These values were calculated from measured values of γ_{ba} and F_{ba} using Eq. (9). Note that W_{ba} for each alcohol-water system is close to 90 ergs/cm². Many years ago, Hardy (16) and then Harkins, Clark, and Roberts (13) reported that W_{ba} for a homologous series of normal aliphatic liquid compounds and water depended primarily on the polar, hydrophilic group of the

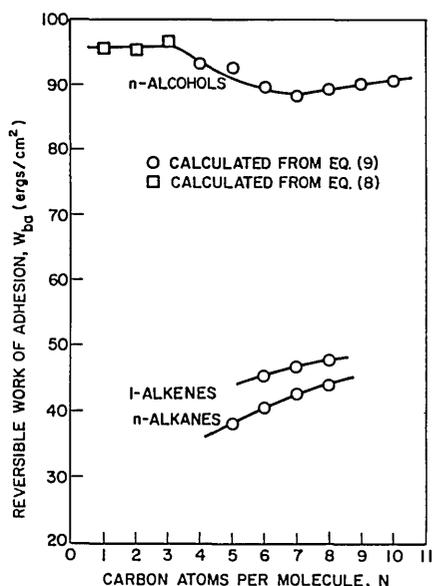


Fig. 4 - Reversible work of adhesion toward water for n-alcohols, n-alkanes, and 1-alkenes at 20°C

properly, that no interface exists between them. Bikerman (17) later described the interfacial tension between organic liquids and water in terms of the difference (Δ) in concentration of organic liquid in the organic phase and the concentration of organic liquid in the aqueous phase. The greater the difference in concentrations, the larger was the interfacial tension.

Donahue and Bartell (15) subsequently related the interfacial tensions between a number of organic liquids and water with the degree of miscibility of the two liquids. They defined the degree of miscibility as the quantity $N_1 + N_2$, where N_1 is the mole fraction of water in the organic phase, and N_2 is the mole fraction of organic liquid in the aqueous phase. When the liquids are completely immiscible $N_1 + N_2$ is zero. As the miscibility of the two liquids increases, $N_1 + N_2$ increases until it is equal to unity, when the liquids are miscible in all proportions. When they plotted $\log(N_1 + N_2)$ against the interfacial tension for each of the liquids studied, a rectilinear plot was obtained except for interfacial tensions less than about 2 dynes/cm.

molecule and so remained practically constant with varying molecular weight. Figure 4 is a plot of W_{ba} for the alcohols against water as a function of N ; it also includes, for comparison, the data of Pomerantz, Clinton, and Zisman (5) for the homologous series of n-alkanes and 1-alkanes against water. The points shown for methanol, ethanol, and 1-propanol were obtained from the Dupré relation, Eq. (8), by letting $\gamma_{ba} = 0$. This figure makes apparent the much greater specific adhesion of the alcohols to water than the nonpolar hydrocarbons. In both families of hydrocarbon liquids W_{ba} decreased monotonically with decreasing chain length. The same effect was observed with the longer chain alcohols; however, as N decreased below 7, the curve passed through a minimum, and W_{ba} began to increase.

Solubility and Interfacial Tension of Surface-Active Compounds

Pound (10) determined the interfacial tensions between a number of organic liquids and water and pointed out that the greater the mutual solubility between the two phases, the lower the interfacial tension. From his observation, it follows that one criterion for the complete miscibility of two liquids is that their interfacial tension be zero or, more

We have plotted our measured interfacial tensions between the n-alcohols and water in an analogous manner and have included the results of Donahue and Bartell for comparison. Since N_1 , the solubility of water in the organic phase, is usually 10 to 100 times as great as N_2 , the reciprocal solubility, we have plotted N_1 as a function of the interfacial tensions. To further broaden our investigation, we have used the initial spreading-pressure measurements reported many years ago by Baker and Zisman (9) and from them calculated the corresponding interfacial tensions according to Eq. (7). All of this information, along with the best available literature data on N_1 and N_2 , have been gathered together in Tables 2 through 5 and plotted in Fig. 5. The measured values shown in this figure include our measured interfacial tensions of the alcohols as well as the data reported by Donahue and Bartell (15); the calculated values represent those calculated from spreading-pressure data using Eq. (7). Figure 5 shows that $\log N_1$ plotted against the interfacial tension is linear. It also shows that the scatter of data points from the plot is no greater for our calculated values of the interfacial tension than that of the best measured values.

It is difficult to attribute the scatter in Fig. 5 to any one cause. Measured interfacial tensions are well known to be highly sensitive to trace, polar, hydrophilic impurities which adsorb at the interface from either liquid phase. Furthermore, the solubility determinations are made difficult because of the experimental problems of distinguishing dissolved from colloiddally dispersed water, the problem of water adsorption on container walls (18), and the solubilization effects which may cause complications if micelle formation occurs. Nevertheless, Fig. 5 allows one to make a convenient approximation of the solubility of water in an organic liquid, if the interfacial tension between the two liquids is known or if it is calculated from the initial spreading pressure upon water. The straight line drawn through the data points in this figure was determined by the method of least squares with equal weight being given to each point. The equation for this line, which may be used to estimate the solubility of water at about 20°C is

$$\log N_1 = -0.226 - 0.0619 \gamma_{ba} . \quad (11)$$

Tables 2 through 5 also include the calculated values for W_{ba} , the reversible work of adhesion per square centimeter of interface, for these various liquids on water. The initial spreading pressure and reversible work of adhesion for each of three homologous series of liquids taken from Table 3 are plotted in Figs. 6 and 7, respectively, as functions of the boiling point; data for the n-alcohols and n-alkanes are included for comparison. The ketones plotted are methyl ethyl ketone, methyl n-butyl ketone, and methyl n-amyl ketone; the acetates are ethyl, n-butyl, and n-amyl acetate; and the ethers are di-n-butyl, di-n-amyl, and di-n-hexyl ether. As was the case with the alcohols, the spreading pressures in each homologous series of compounds increased as the normal boiling point decreased. This corresponds to an increase in spreading pressure with increasing mutual solubility. The ketone and acetate families also reached a theoretical maximum spreading pressure, analogous to that of the alcohols, when the solubility increased to the extent that the interfacial tension between the organic liquid and water vanished.

The curves in Fig. 7 of the reversible work of adhesion vs boiling point for the ketones, acetates, and ethers each resemble that of the alcohol family in that the curves connecting the lower boiling liquids have negative slopes. Although the curve for each of these families shows no minimum, as did the alcohol curve, the shape suggests that it would have a minimum if data for the higher boiling homologs were available. In contrast to these homologous families, the n-alkane curve has a consistently positive slope.

It is possible to explain qualitatively the shapes of the curves in Fig. 7 if the molar work of adhesion (ω_{ba}) is considered. This quantity may be calculated from W_{ba} using the following relation given by Pomerantz, Clinton, and Zisman (5):

Table 2
Surface Tension, Spreading Pressure, Work of Adhesion, and Solubility Data for Various Alcohol-Water Systems
(All values at 20°C except when otherwise specified)

Liquid	γ_b (dynes/cm)	$F_{b,a}$ (dynes/cm)	$\gamma_{b,a}$ (dynes/cm)		$W_{b,a}^*$ (ergs/cm ²)	Mole Fraction	
			Measured	Calculated		N_1	N_2
1-Butanol	24.27	44.8	1.8 ²⁵ † 2.84	— 3.68	— 93.34	0.500 ²⁵ † 0.500 ²⁵ †	0.0188 ²⁵ ‡§ 0.0188 ²⁵ ‡§
2-Butanol	23.47¶	50.4**	—	-1.12	97.3	0.5††	—
2-Methyl-1-propanol	22.9¶	49.3**	2.0 ²⁵ †	0.55	95.1	0.449 ²⁵ †	0.0195 ²⁵ †
1-Pentanol	24.90	42.5	4.4 ²⁵ † 5.33	— 5.35	— 92.30	0.357 ²⁵ † 0.357 ²⁵ †	0.00459 ²⁵ ‡§ 0.00459 ²⁵ ‡§
Isoamyl alcohol	—	—	4.8 ²⁵ †	—	—	0.326 ²⁵ ‡††	0.0055 ²⁵ ‡††
1-Hexanol	25.66	38.1	6.8 ²⁵ † 8.94	— 8.99	— 89.42	0.288 ²⁵ † 0.288 ²⁵ †	0.00110 ²⁵ ‡ 0.00110 ²⁵ ‡
2-Ethyl-1-butanol	25.95¶	39.1**	—	7.75	90.9	0.213††	—
1-Heptanol	26.09	36.1	7.7 ²⁵ † 9.78	— 9.76	— 88.28	0.267 ²⁵ † 0.267 ²⁵ †	0.00028 ²⁵ ‡ 0.00028 ²⁵ ‡
Cyclohexanol	33.15 ^{33.5} ¶	31.5**	3.9 ^{16.2} §§	—	97.8	0.406 ²⁵ ‡††	0.008 ²⁵ ‡††
Methyl cellosolve	33.0 ²⁸ ¶¶	41.2**	—	-1.45	107.2	0.5††	—
Cellosolve	29.5 ²⁸ ¶¶	40.2**	—	3.05	99.2	0.5††	—
Diethyl carbitol	26.99 ²² ¶	39.6**	—	6.16	92.5	0.5††	—

*Calculated from Eq. (9).

§§ From Ref. 23.

† From Ref. 15.

¶ From Ref. 24.

‡ From Ref. 19.

¶ From Ref. 24.

§ From Ref. 20.

¶ From Ref. 12.

** From Ref. 9.

†† From Ref. 21.

‡‡ From Ref. 22.

Table 3
Surface Tension, Spreading Pressure, Work of Adhesion, and Solubility Data for
Various Hydrophilic Organic Liquid-Water Systems
(All values at 20°C except where otherwise specified)

Liquid	γ_b (dynes/cm)	$F_{b,a}$ (dynes/cm)	$\gamma_{b,a}$ (dynes/cm)		$W_{b,a}$ * (ergs/cm ²)	Mole Fraction	
			Measured	Calculated		N_1	N_2
Ethers							
Diisopropyl ether	18.4 ¹⁴ †	31.2 §	—	23.16	—	0.0333 ²⁵ †	0.00187 ²⁵ †
Di-n-butyl ether	22.90 †	24.7 §	—	25.15	68.0	0.0315 ¶	0.00187 ²⁵ †
Di-n-amyl ether	24.76 †	18.1 §	—	29.89	70.5	0.0136 ¶	—
Di-n-hexyl ether	24.51 ²⁵ †	17.2 §	—	31.04	67.6	0.0126 ¶	—
	24.51 ²⁵ †	17.2 §	—	31.04	66.2	0.0123 ¶	—
					66.2	0.0099 ²⁷ **	—
Ketones							
Methyl ethyl ketone	24.6 †	46.2 §	—	1.95	95.4	0.5 ¶	—
Methyl n-propyl ketone	22.41 ²⁵ †	—	6.3 † †	—	88.8 † †	0.152 ²⁵ §§	0.0132 ²⁵ §§
Methyl n-butyl ketone	25.32 ²¹ †	37.6 ¶	9.6 ²⁵ †	9.8	88.2	0.176 ²⁵ §§	0.0050 ²⁵ §§
Methyl n-amyl ketone	—	—	12.4 ²⁵ †	—	—	0.123 ²⁵ §§	0.0031 ²⁵ §§
Diisobutyl ketone	26.20 ²⁴ †	35.8 §	—	10.75	88.2	0.0881 ¶	0.0031 ²⁵ §§
Acetyl acetone	23.92 ²² †	26.8 §	—	22.03	74.6	0.0344 ¶	0.000076 ¶
	30.26 ¹⁷ †	31.9 §	—	10.59	92.4	0.225 ³⁰ §§	0.0318 ³⁰ §§
Esters							
Ethyl acetate	23.75 †	41.9 §	6.8 ²⁵ †	—	—	0.139 ²⁵ §§	0.0163 ²⁵ §§
n-Butyl acetate	25.21 ²¹ †	34.1 §	14.5 ²⁵ †	7.10	89.4	0.143 ¶	0.0163 ²⁵ §§
n-Amyl acetate	25.68 †	31.1 §	—	13.44	84.5	0.0745 ²⁵ †	0.000995 ²⁵ †
			—	15.97	82.5	0.137 ²⁵ §§	0.00363 ²⁵ §§
			—	—	—	0.0351 ¶	0.00024 §§

*Calculated from Eq. (9).

†From Ref. 15.

‡From Ref. 12.

§From Ref. 9.

¶From Ref. 21.

**From Ref. 18.

††From Ref. 13.

‡‡Calculated from Dupre relation, Eq. (8).

§§From Ref. 22.

¶¶From Ref. 1.

Table 4
Surface Tension, Spreading Pressure, Work of Adhesion, and Solubility Data for
Various Hydrocarbon-Water Systems
(All values at 20°C except where otherwise specified)

Liquid	γ_b (dynes/cm)	$F_{b,a}$ (dynes/cm)	$\gamma_{b,a}$ (dynes/cm)		$W_{b,a}^*$ (ergs/cm ²)	Mole Fraction	
			Measured	Calculated		N_1	N_2
n-Pentane	15.98 †	5.90**	49.0 ²⁵ †	—	—	0.00048 ²⁵ †	0.00015 ²⁵ §
n-Hexane	18.42 †	3.70**	49.7 ²⁵ †	50.8	37.86	0.00036 †	0.0000095 ††
n-Heptane	—	—	—	50.73	40.54	0.00060 ²⁵ †	0.000029 ²⁵ §
n-Octane	20.26 †	1.80**	50.2 ²⁵ †	—	—	0.00053 †	0.0000019 ††
	20.26 †	1.80**	—	50.69	42.32	0.00084 ²⁵ †	0.000009 ²⁵ §
	—	—	—	50.69	42.32	0.00073 †	0.0000005 ††
	21.80 †	0.10**	50.2 ²⁵ †	—	—	0.00051 ††	0.0000005 ††
	21.80 †	0.10**	—	50.85	43.70	0.00090 ²⁵ †	0.000003 ²⁵ §
2-Methyl butane	14.97 †	7.70**	—	50.08	43.70	0.00090 †	0.0000001 ††
Cyclohexane	24.95 †	—	—	—	37.64	0.00056 ³² §§	0.0000001 ††
Benzene	28.88 †	9.8**	50.0 ²⁵ †	—	47.7 ††	0.00037 §	0.000012 ††
	—	—	34.1 ²⁵ †	—	—	0.00055 ²⁵ §	0.000022 ²⁵ §
Ethyl benzene	29.04***	6.1**	—	34.07	67.56	0.0031 ²⁵ †	0.00042 ²⁵ †
Toluene	28.52 †	—	38.4 ²⁵ †	—	—	0.0024 †	0.00041 ††
Xylene	—	—	—	37.61	64.18	0.0023 ²⁵ §	0.000025 ²⁵ §
	—	—	36.1 ²⁵ †††	—	65.17 ††	0.0019 †	0.000026 ††
	—	—	37.2 ²⁵ †	—	—	0.0025 ²⁵ §	0.00010 ²⁵ §
	—	—	—	—	—	0.0023 ²⁵ §	0.000024 ²⁵ §

*Calculated from Eq. (9).

†From Ref. 15.

‡From Ref. 25.

§From Ref. 22.

¶From Ref. 12.

**From Ref. 5.

††From Ref. 26.

‡‡From Ref. 27.

§§From Ref. 18.

¶¶Calculated from Dupre relation, Eq. (8).

***From Ref. 28.

†††From Ref. 29.

Table 5
Surface Tension, Spreading Pressure, Work of Adhesion, and Solubility Data for
Some Miscellaneous Organic Liquid-Water Systems
(All values at 20°C except where otherwise specified)

Liquid	γ_b (dynes/cm)	$F_{b,a}$ (dynes/cm)	$\gamma_{b,a}$ (dynes/cm)		$W_{b,a}^*$ (ergs/cm ²)	Mole Fraction	
			Measured	Calculated		N_1	N_2
Ethyl bromide	24.15 [†]	—	31.3 ^{25°†}	—	65.6	0.0048 ^{25°†}	0.0015 ^{25°†}
Methylene chloride	—	—	28.0 ^{25°†}	—	—	0.0113 ^{25°§}	0.0042 ^{25°§}
Chloroform	27.14 [†]	—	31.6 ^{25°†}	—	68.3	0.0050 ^{25°§}	0.0012 ^{25°§}
Carbon tetrachloride	25.68 [†]	—	43.7 ^{25°†}	—	54.7	0.00083 ^{25°†}	0.000097 ^{25°†}
Nitromethane	36.97 [†]	—	9.5 ^{25°†}	—	100.2	0.082 ^{25°§}	0.025 ^{25°§}
Carbon disulfide	—	—	48.1 ^{25°†}	—	—	0.00070 ^{25°§}	0.00028 ^{25°§}
Bromobenzene	36.34 [†]	—	38.1 ^{25°†}	—	71.0	0.0029 ^{25°†}	0.000053 ^{25°†}
Nitrobenzene	43.35 [†]	—	25.2 ^{25°†}	—	90.9	0.0175 ^{25°†}	0.000295 ^{25°†}
Aniline	39.97 [†]	—	5.8 [†]	—	106.9	0.216 ^{25°§}	0.0132 ^{25°§}

*Calculated from Dupré relation, Eq. (8).

†From Ref. 12.

‡From Ref. 15.

§From Ref. 22.

¶From Ref. 13.

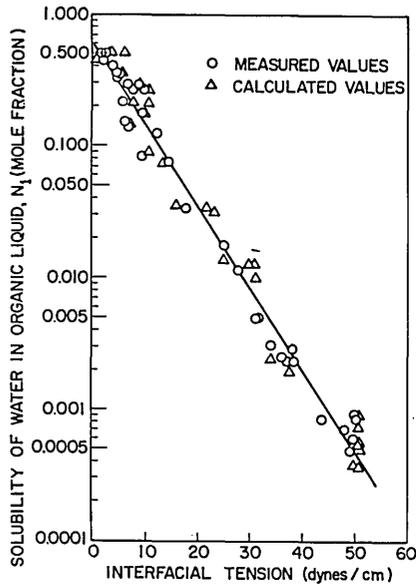


Fig. 5 - Solubility as a function of interfacial tension

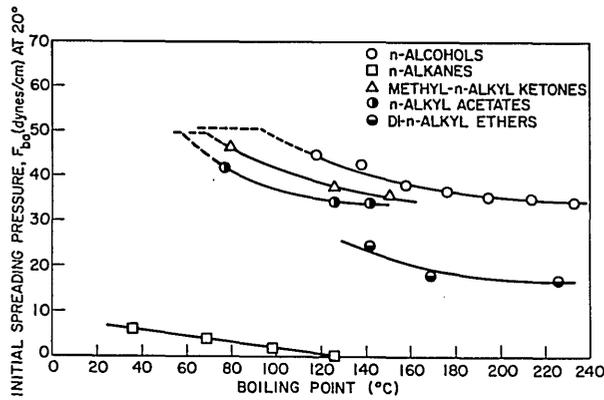


Fig. 6 - Spreading pressures of some organic liquids on water vs boiling point

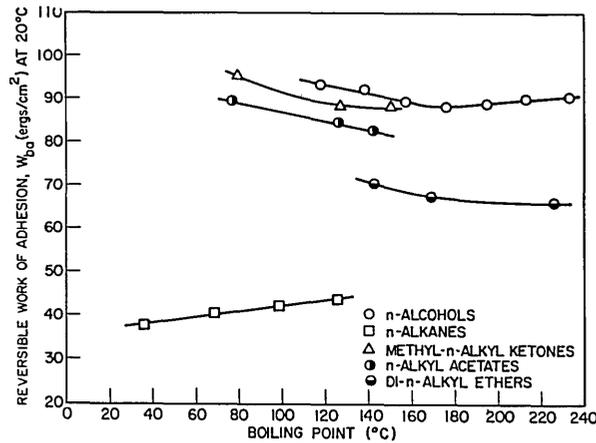


Fig. 7 - Reversible work of adhesion for some organic liquids with water vs boiling point

$$\omega_{b_a} = \frac{W_{b_a} \sigma_b (6.02 \times 10^{23})}{4.18 \times 10^7}, \quad (12)$$

where σ_b is the area occupied per organic molecule at the organic liquid-water interface. Equation (12) can be solved for W_{b_a} , and it can be seen that W_{b_a} is directly proportional to ω_{b_a} and inversely proportional to σ_b .

Since the n-alcohol molecules have linear structures with terminal hydrophilic groups, which are strongly hydrogen bonded to water, they will, under surface pressure, tend to orient at the water interface with the principal axis of the molecular chain in the vertical direction. Films composed of molecules of this type show an increase in σ_b as the molecular chain becomes shorter (boiling point decreases), because a vertical orientation becomes less common and more randomness develops as the intermolecular cohesive forces between paraffinic chains diminish. As σ_b increases, W_{b_a} will tend to decrease. This is probably the reason for the positive slope of the W_{b_a} -vs-boiling-point curve of the higher alcohols. However, as the boiling point decreases further and the alcohols become much less well aligned, each molecule becomes associated with, or surrounded by, more molecules of water; hence, these alcohol-water aggregates (or mixed alcohol-water films) begin to become more like the water substrate. This causes a rapid increase in ω_{b_a} as it approaches ω_{a_a} , the molar work of cohesion of water. The portion of the alcohol curve having a negative slope is probably caused by this effect; i.e., ω_{b_a} increases at a greater rate than σ_b , resulting in a net increase in W_{b_a} .

The methyl n-alkyl ketones and n-alkyl acetates, because the polar group in each molecule is only one carbon atom removed from the end of the chain, are still able to orient at the water surface in a nearly vertical position. However, they are more weakly hydrogen bonded to the water substrate than the n-alcohols. This fact, together with the rapid increase in water solubility of the lower homologs as N decreases, allows one to describe the shape of these curves in the same manner as the alcohol curve.

The di-n-alkyl ethers, having a bent molecular chain with the polar group located at the center, are unable to orient and pack at the water interface as well as the alcohols. In addition, the diethers are even more weakly hydrogen bonded to water. Consequently, these ethers are unable to orient and close-pack efficiently. These molecules would be expected to exhibit a decrease in σ_b as the boiling point decreases. Therefore, there should be a negative slope of the ether curve, since ω_{b_a} would then tend to increase. Any effect of water penetration into the ether film would also enhance this trend.

The W_{b_a} -vs-boiling-point curve for the n-alkanes has a positive slope over its entire length, and W_{b_a} decreases regularly with decreasing boiling point. Pomerantz, Clinton, and Zisman (5) attributed this decrease to a regular decrease in ω_{b_a} as fewer methylene groups of these horizontally oriented molecules were present at the water interface. This explains the decrease in W_{b_a} as long as σ_b does not change appreciably. Because the alkanes had very low spreading pressures, there was insufficient surface pressure on the adsorbed alkane molecules to close-pack and orient them at the water interface. Hence, we can understand why each molecule assumed nearly the same σ_b .

Figure 7 illustrates clearly the differences in affinity of the various polar groups for water. An evident generalization from these data is that the reversible work of adhesion decreases in the order alcohols > ketones > esters > ethers > alkanes. Here again, each family shows only a small change in W_{b_a} from one homolog to another; the magnitude of these values is determined primarily by the polar group and not by the size or length of the molecule.

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13. ABSTRACT An investigation has been made of the effect of chain length and solubility upon the spreading on water of the homologous series of pure normal alcohols from 1-butanol to 1-decanol. Spreading pressures were measured at 20°C using the piston-monolayer method. Each measured value corresponded to the semi-initial spreading pressure, which was equal, within experimental error, to the initial spreading pressure. Surface tensions of these alcohols were measured, as were the interfacial tensions with water. It is concluded that the spreading pressure of each alcohol, together with its surface tension, can be used to calculate reliably the interfacial tension and the reversible work of adhesion to water. Data for the spreading pressures on water of a variety of organic liquids are also given. With these data and literature values of the liquid surface tensions, calculations were made of the interfacial tensions and work of adhesion by means of the equations published by Pomerantz, Clinton, and Zisman. The calculated interfacial tension was plotted as a function of the best available literature value of the solubility of water in each organic liquid. Our results agreed well with Donahue and Bartell's logarithmic relationship between the interfacial tension and the degree of miscibility. A relationship is given from which solubility can be estimated from interfacial tension. Finally, the relation between the molar work of adhesion to water and the constitution of the adsorbed organic molecules is discussed.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polar organic compounds Initial spreading coefficient Spreading pressure Interfacial tension Work of adhesion Solubility Miscibility Surface chemistry						