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PREVIEW

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SPREADING PRESSURES AND SPREADING COEFFICIENTS  
OF CERTAIN HYDROCARBONS ON WATER

by

James Edward Shewmaker

A THESIS

Presented to the Faculty of  
The Graduate College in the University of Nebraska  
In Partial Fulfillment of Requirements for the  
Degree of Doctor of Philosophy  
Department of Chemistry

Under the Supervision of Dr. E. R. Washburn

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PREVIEW

## TABLE OF CONTENTS

	Page
I. Introduction. . . . .	1
II. Materials . . . . .	10
III. Apparatus . . . . .	21
IV. Experimental. . . . .	30
A. Measurement of Surface Tension. . . . .	30
B. Measurement of Interfacial Tension. . . . .	36
C. Measurement of Spreading Pressure . . . . .	44
D. The Spreading of Tetralin . . . . .	59
E. Comparison of Spreading Coefficients and Spreading Pressures . . . . .	66
V. Discussion of Results . . . . .	68
VI. Additional Observations . . . . .	95
A. The Effect of Water Dissolved in the Organic Liquids upon their Spreading Pressure. . . . .	95
B. Determination of Spreading Pressure from Surface Tension Measurements by the Ring Method. . . . .	105
VII. Summary . . . . .	113
Bibliography. . . . .	114



## I. INTRODUCTION

### A. Spreading Coefficients

Although the phenomenon of a liquid spontaneously spreading upon a horizontal surface has been familiar for a long time, Harkins and co-workers<sup>1,2,3</sup> appear to have been the first to present a comprehensive theory treating this behavior. This theory has been modified and extended by Harkins and Ginsberg,<sup>4</sup> Harkins,<sup>5,6,7</sup> and Miller<sup>8</sup> to cover all degrees of spreading of any liquid or solid upon any uniform surface.

Qualitative statements of the requirements for spreading had been given previously, but none had been generally accepted. The Neumann triangle of forces<sup>9</sup> led to the conclusion that a liquid B will spread upon a liquid A if  $ST_A > ST_B + IT_{AB}$ , where  $IT_{AB}$  represents the interfacial tension between the two liquids, and  $ST_A$  and  $ST_B$  the respective surface tensions. The condition for non-spreading was  $ST_A < ST_B + IT_{AB}$ . This assumed the surface tension of the sub-phase to be equivalent to a force in one direction, and the surface tension of the spreading liquid, together with the interfacial tension, to be equivalent to forces in the opposite direction. An unbalanced force was assumed to displace the edge of the added drop of liquid B. This formulation was concerned only with whether or not spreading would occur.

Studies by Lord Rayleigh<sup>10</sup> led him to the conclusion that all liquids spread on the surface of clean water. He concluded that whenever there was apparently a case of

non-spreading, it was caused by contamination on the surface.

Another generalization concerning spreading and non-spreading was proposed by Langmuir.<sup>11,12</sup> According to this view only those liquids whose molecules are polar or contain polar groups, spread on water. Hence, Langmuir claimed that pure hydrocarbons would not spread upon water.<sup>13</sup> Hardy had previously reported that pure saturated hydrocarbons did not spread upon water surfaces.

The theory of Harkins<sup>1</sup> defines a single quantity for each liquid which is a measure of its tendency to spread upon a given surface. This characteristic quantity, developed entirely from the thermodynamics of surfaces, is called the spreading coefficient of the given liquid upon the given surface. Fortunately, it bears a simple relationship to the surface tensions of the spreading material and the sub-phase and the interfacial tension between these substances. It can, therefore, be calculated for any system for which these three boundary tensions are known or can be measured. The fact that no satisfactory procedure has yet been devised to measure boundary tensions involving solid surfaces, limits this theory only in its experimental applications to these materials. Considering the great abundance and importance of processes involving films and film formation upon solid surfaces, this experimental limitation is indeed a very serious one but does not affect the validity of the theory.

Harkins' method of predicting the tendency of a substance to spread is based on the changes in free energy involved in

the spreading and the universal tendency of all systems to approach a state of minimum free energy. When a liquid B spreads over a liquid A with which it has a low mutual solubility, the liquid-air interface of A is replaced by the liquid-air interface of B and the liquid-liquid interface of A and B. The changes in area of the three interfaces are approximately equal. Since surface tension is the mathematical equivalent of the free surface energy per unit area of surface, the net change in free surface energy due to each square centimeter of spreading ( $\Delta FSE'$ ) is given by the expression,

$$\Delta FSE' = ST_A - ST_B - IT_{AB} \quad (1)$$

where,  $ST_A$  and  $ST_B$  represent the respective surface tensions of the underlying and the spreading liquid and  $IT_{AB}$  is the interfacial tension between these liquids as bulk phases.

The requirement for spontaneous spreading starting from any given condition is,

$$\Delta FSE' < 0. \quad (2)$$

When,  $\Delta FSE' > 0, \quad (3)$

spontaneous spreading will not occur.

Harkins<sup>4</sup> designated the decrease in free surface energy per square centimeter of spreading as the spreading coefficient, SC. Harkins' spreading coefficient is, therefore, given by the equation,

$$SC = ST_A - (ST_B + IT_{AB}), \quad (4)$$

The value of the spreading coefficient is calculated by this equation from measured surface and interfacial tensions.

There are at present no experimental methods for measuring spreading coefficients directly. A large positive value for the spreading coefficient indicates that the rate of change of the free surface energy with the area of spreading has a large negative value and, therefore, the thermodynamic spreading potential for substance B upon surface A is large. When SC is equal to or less than zero, B will not spread upon A.

Since surface and interfacial tensions are characteristic, at any given temperature, of the substances forming the phase boundaries, it is apparent that spreading coefficients calculated by equation (4) from these properties are also characteristic of a particular liquid spreading upon a given surface at any given temperature. The spreading coefficient is derived entirely from surface and interfacial tensions and, hence, may likewise be expressed in dynes per centimeter.

#### B. Spreading Pressures

The term "spreading pressure" designates the force per centimeter length of restraining barrier exerted as one substance spreads upon the surface of another. It is usually expressed in dynes per centimeter, the same dimensions as used for the spreading coefficient. Unlike the spreading coefficient, it is measured directly. It has been found that the spreading pressure of a liquid upon a particular surface at a given temperature is a definite, characteristic and reproducible property.<sup>8,9,11,14,15,16,17,18</sup> The spreading



coefficient and the spreading pressure of a substance are independent quantitative expressions of the tendency of that substance to spread upon a given surface at a specified temperature.

Soon after the idea of surface tension became established, it was noted that oil placed upon water lowered its surface tension. Rayleigh<sup>19</sup> appears to have been the first to make accurate measurements of the lowering of the surface tension of water by films of oil. Pockels<sup>20</sup> made the important discovery that surface films can be handled by pushing them in front of strips or barriers extending the whole width of a trough of water filled to the brim. Thus, not only could the films be confined to any desired area but the surface could also be cleaned by sweeping. Rayleigh<sup>21</sup> then used this technique to investigate the relation of the surface tension decrease caused by oil films upon water to the degree of compression of the films. In these studies it was found that if the area available to the film exceeded a certain critical amount for a given quantity of oil, the surface tension of the water was not lowered and movements of the barrier had no effect. But, if the area was diminished below this critical amount, the surface tension fell rapidly. Rayleigh's calculations of the thickness of the oil films at this critical area showed the films to be one molecule deep. Many other investigators<sup>9,11,22</sup> have found films of a large number of organic compounds upon water to be monomolecular. No case appears to have been found where pure chemical substances

have formed uniform films more than one molecule deep.

The first direct measurements of the outward surface pressure exerted by a spreading liquid were made by Langmuir<sup>11</sup> in 1917. He used a tray filled to the brim with water and paper barriers for cleaning the surface and compressing the films similar to Pockels' arrangement. The new feature of his apparatus was a floating barrier laid across the water surface but not quite touching either edge of the tray. The film was kept from flowing around the ends of this float by two jets of air. This float pressed on two nearly vertical rods attached to an ordinary balance. The force exerted upon this floating barrier could thus be measured. Drops of a non-volatile spreading liquid when added to a limited area of the surface, trapped between a fixed barrier and the float, spread out to cover the available area with a monomolecular film. Then the spreading force was transmitted to the float by this stable monomolecular film of the spreading liquid. This force per centimeter length of the barrier is the spreading pressure of the liquid upon water. Though his apparatus has been extensively modified, the same principle is still generally used in measuring spreading pressures.

The actual spreading pressures for several non-volatile liquids have been measured and compared to the spreading coefficients calculated by Harkins.<sup>8,15,23,24,25</sup>

An important extension of the use of the surface film balance in measuring spreading pressures is due to Washburn

17  
and Keim. These investigators introduced a technique for measuring the spreading pressure of volatile liquids on water. In this new procedure, a monomolecular film of some long-chain substance containing both a polar and a non-polar group (such as stearic acid) was floated upon the surface of water in the tray of the surface film balance. This film was compressed by moving a barrier along on the surface of the water.

To make a determination of spreading pressure, the film was placed under slight lateral compression and a small amount of the liquid whose spreading was being studied was added to the surface. The added liquid penetrated the film and spread upon the water, thus further compressing the restraining monofilm. It was found that the maximum force exerted upon the float of the balance as the liquid spread was independent of the initial state of compression of the restraining film. The magnitude of this spreading force was also the same whether stearic acid, palmitic acid, or tristearin monofilms were used to transmit it to the float. The force exerted per centimeter length of the float (in dynes/cm.) while the spreading volatile liquid remained upon the water was characteristic of the liquid and the temperature and was considered to be the spreading pressure value of that liquid upon water at the given temperature.

The spreading pressure values (at 25°C.) of Washburn  
17  
and Keim, with the exception of iso-amyl chloride, did not differ by more than about one dyne per centimeter from spreading coefficients which Harkins and Feldman<sup>1</sup> had previously

calculated for the same liquids on water (at 20°C.).

<sup>26</sup>  
Kahler used the vertical pull type film balance to measure the spreading pressure of volatile liquids by restraining their spreading with monomolecular films of palmitic or stearic acid.

<sup>18</sup>  
Washburn, Transue and Kahler were the first to make a careful comparison of spreading pressures, measured directly by the method of Washburn and Keim, to the spreading coefficients calculated from surface and interfacial tension values measured upon the same samples of volatile liquids at the same temperature. For carefully purified samples of benzene, toluene, acetophenone and iso-amyl chloride, these workers found that the spreading pressures exerted by these liquids as they spread to form monomolecular layers on water agreed within  $\pm 0.1$  to  $\pm 0.6$  dynes/cm. with the spreading coefficients calculated from surface and interfacial tensions measured upon the bulk phases.

It has been the primary purpose of this investigation to make an accurate comparison of the spreading pressures and spreading coefficients of several purified hydrocarbons of varying volatility upon water, in order to determine with what accuracy spreading coefficients actually predict the spreading tendencies. The experiments performed in this research also served to further evaluate the method of Washburn and Keim <sup>17</sup> for the direct measurement of spreading pressures upon water. Spreading pressures have been measured by Washburn and Keim's procedure. Surface tensions and interfacial tensions



have been determined by the capillary rise methods since these are the most accurate methods known and the most sensitive to surface-active impurities which if present but undetected would most likely invalidate the intended comparisons. All three measurements have been made upon identical samples of the liquids and at the same temperature.

Benzene was the first liquid studied in all three of the basic measurements. Reliable values for its surface tension, interfacial tension, and spreading pressure had already been reported. Good agreement between the measurements by the author and literature data were considered to indicate a satisfactory condition of the apparatus and that the technique of performing the measurements was also satisfactory. The alkylbenzenes were selected for study in order to determine the effects of various structural changes in the alkyl side chains upon surface and interfacial tensions and their spreading pressures upon water.

## II. MATERIALS

All of the liquids used in this investigation, with the exceptions of benzene and tetralin, were of the white-labelled highest purity grade of the Eastman Kodak Company. It was therefore expected that perhaps some of the liquids could be used as obtained. In addition to refractive index and density, the surface tension values and the constancy of the interfacial tensions of the liquids were used as criteria of purity. Since even slight amounts of many impurities cause marked changes in surface and interfacial tensions, as measured by the capillary rise method, with time, the constancy and reproducibility of these measurements were considered to be excellent indications of purity. Therefore, in surveying these materials, their refractive indices and densities were first determined and compared to literature values. If these checked, their surface tensions were measured and compared to literature data where reported. If a liquid met all these tests, its interfacial tension was investigated. In general, interfacial tension is a more sensitive indicator of a surface-active impurity than surface tension so that it was sometimes necessary, even though a liquid gave excellent surface tension values, to extract the liquid with water or to resort to more elaborate purification before reproducible interfacial tension measurements were possible. The extractions were carried out by vigorously shaking the liquid in question with several milliliters of freshly distilled water, allowing it to stand for several hours, then pumping off the liquid

from the center of the organic phase without disturbing the interfaces.

#### A. Benzene

Analytical reagent grade benzene (thiophene free) was purified by four fractional crystallizations. In each crystallization nine-tenths of the liquid was frozen in a calcium chloride-ice bath and the remaining tenth drained off. The range of freezing points for this purified benzene was 5.54 to 5.52°C. No detectable coloration developed after twenty-four hours contact with concentrated sulfuric acid. The benzene purified in this manner gave satisfactory surface tension values. However, it was necessary to extract the benzene with water several times before constant interfacial tension values could be obtained. The physical properties of this purified benzene are listed in Table I.

#### B. Ethylbenzene

The best grade obtainable from Eastman Kodak Company was used as received after it was found that its refractive index, density and surface tension values compared favorably with those reported in the literature. It was necessary to extract the liquid with water several times in order to obtain interfacial tension values that were reproducible and constant with time. Table I allows a comparison of the physical properties of this liquid with literature values.

### C. n-Propylbenzene

The best grade from Eastman Kodak Company was obtained but a study of its physical properties showed that it could not be used as received. This liquid was purified by two careful fractional distillations under reduced pressure in an all glass apparatus employing a 24-inch Vigreux column. Since this liquid was quite expensive the following scheme was used to follow the progress of the fractionation. The distillate was collected in 4-8-ml. portions and the refractive indices of the bulk of each fraction and of the last drops of each distillation taken from the condenser tube were measured. The refractive index of the original sample was about 0.0010 low but the refractive indices of the earlier fractions were much lower than that of the original liquid. After a few small fractions had been removed, their refractive indices began to climb. When the refractive index had thus risen to within 3 in the fourth place of the literature value, a large fraction was taken. After this large fraction was removed, small fractions were collected again as long as the refractive index was equal or just slightly below the correct value and all these portions having refractive indices within 3 in the fourth decimal place of the correct value were combined for a second fractionation. In all, a total of 22 fractions were taken in the first distillation. The second fractionation was carried out in a similar manner except that fewer fractions were required before the refractive index indicated the liquid to be of

satisfactory quality. The fraction that was collected for experimentation distilled at a temperature of  $46.2^{\circ}$  to  $46.4^{\circ}\text{C}$ . at a pressure of 10.0 to 10.1 mm. The physical properties of the n-propylbenzene, purified in this manner, are recorded in Table I.

#### D. iso-Propylbenzene

The best grade obtainable from Eastman Kodak Company was used as received since its refractive index, density and surface tension agreed well with literature values. The density, refractive index and surface tension of this iso-propylbenzene are given in Table I.

#### E. n-Butylbenzene

The original sample of this liquid was Eastman's best grade. The need for further purification was indicated by the fact that the measured density was 0.0010 too large and the impossibility of getting interfacial tension measurements which were constant with time. After fifteen extractions with water, this liquid still did not give constant interfacial tension values. Preliminary attempts to purify this liquid by drying over sodium and by extraction with concentrated sulfuric acid only gave poorer values for density and refractive index.

This liquid was purified by two successive fractional distillations under reduced pressure using the same apparatus and the same general procedure as described for n-propylbenzene. About 300 ml. of liquid were taken for purification



and about 125 ml. were collected in the "best" fraction of the second distillation. This selected fraction distilled at a temperature of  $67.0^{\circ}\text{C}$ . under a pressure of 11.0 mm. and the refractive index of the first and last drops of the distillate differed no more than 2 in the fourth decimal place. After this purification, the n-butylbenzene exhibited the physical properties recorded in Table I.

#### F. sec-Butylbenzene

Eastman's best grade was used as received since measured density, refractive index and surface tension agreed satisfactorily with literature values. The physical properties of this material are given in Table I. After several extractions with water this liquid gave reproducible interfacial tension measurements.

#### G. tert-Butylbenzene

The best grade of tertiary butylbenzene obtainable from Eastman Kodak Company was used as received. The density, refractive index, and surface tension agreed well with literature values as shown in Table I. Furthermore, this liquid gave constant interfacial tension values which were not changed by extraction with water.

#### H. Tetralin (1,2,3,4-tetrahydronaphthalene)

Practical grade tetralin was purchased from the Eastman Kodak Company. One kilogram of this liquid was taken for

purification. It was slowly frozen with occasional shaking in a slush of dry ice and alcohol. After two fractional crystallizations, in each of which about nine-tenths of the original volume was frozen and the remaining tenth poured off, the refractive index and density showed only slight improvement. Efforts were then directed to purifying this liquid by reduced pressure fractional distillation from freshly-cut sodium. These distillations were carried out in the same apparatus and following the same procedure described for *n*-propylbenzene. The tetralin after two such successive fractional distillations had the physical properties listed in Table I. The fraction collected for further study distilled at a temperature of 86.8° to 87.1°C. under a pressure of  $13.0 \pm 0.5$  mm.

During the course of this research, it was discovered that this purified sample suffered peroxidation upon exposure to light. It was therefore necessary to re-purify this liquid before all measurements. These purifications are described in the "Experimental" section of this thesis.

#### I. iso-Octane (2,2,4-trimethylpentane)

The sample of iso-octane used in this study was Eastman's Spectro grade. Its physical properties are compared to literature values in Table I. This liquid gave surface tension values which were constant with time and after a few extractions with water gave reproducible interfacial tension values also.

## J. Stearic Acid

The best grade obtainable from Eastman Kodak Company was used. Many workers in this laboratory have found this sample to be sufficiently pure for use as the restraining film material for hydrophil balance measurements. The stearic acid was applied to the water surface of the film balance as a dilute solution in benzene (about 0.0005 g. stearic acid per cc. of benzene). Applied in this way to a sufficiently large area, the benzene quickly evaporated leaving a monomolecular film of stearic acid.

## K. Water

The water used in this investigation was obtained from two different sources. That used in the hydrophil balance and for intermediate rinsings in the cleaning of glassware was obtained by distillation of tap water from a continuous overflow type of all-metal still. The water was stored in a twenty-liter bottle which had been used for this purpose for several years. This water has been found in the course of many measurements to be satisfactory for this use. Its surface tension at  $25.00^{\circ}\text{C}$ . as measured by capillary rise was  $72.11 \pm 0.04$  dynes/cm. Measurements of its specific resistance at  $25^{\circ}\text{C}$ . varied between 640,000 and 700,000 ohm centimeters.

The water used for all interfacial tension work and for final rinsings of all glassware was obtained from the