[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Spreading of Volatile Organic Liquids on Water in the Presence of Unimolecular Films

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It has been observed that liquids which ordinarily spread on water may not do so if a surface impurity is present on the water.[2,3]

Observers in this Laboratory have noted that a drop of a liquid like benzene, if allowed to fall on a unimolecular surface film floating on water, would penetrate the film and spread on the water, pushing the film back if the original compression of the film was not great. If, by means of a movable barrier, the unimolecular film was compressed to some extent the benzene spread much less than it did with the uncompressed film. A somewhat greater pressure on the film entirely prevented the spreading of the benzene. Under such conditions the benzene drop appeared to float in the form of a thin lens on top of the unimolecular film.

If the added liquid was less dense than water, as is benzene, it was found that when a drop was released beneath the surface of the water it would rise to the interface between the water and the film where it was delayed for a short time before erupting through the film. The actual spreading behavior was then no different than when the drop was added from above.

Several different films were employed in the preliminary investigation. The minimum pressure at which no spreading of a given liquid occurred did not appear to vary with the film among the films employed.

From these observations it is apparent that we have here phenomena which lead to the direct and possibly precise measurement of the tendencies of different liquids to spread on water.

This method may be looked upon as a modification of the use of non-volatile oils as indicator or piston oils described by Cary and Rideal,[4] Blodgett,[5] Langmuir and Schaefer[6] and others. They employed relatively large quantities of these oils on water to exert a definite pressure through a unimolecular film. Frequently they used a waxed thread to separate the piston oil from the unimolecular film. In the method here proposed a few drops of volatile liquid added directly upon the film permit the measurement of spreading tendency. It is apparent that non-volatile liquids also can be used. With this idea in mind the following quantitative measurements have been made.

Materials.—Unimolecular film materials: palmitic acid, stearic acid and tristearin from Eastman Kodak Company dissolved in analytical grade benzene were used to form the films.

Spreading materials—nitrobenzene: ordinary reagent was dried by anhydrous calcium chloride and then distilled. The middle portion was collected and recrystallized, f. p. 5.6°, n^{20}D 1.5528.

Benzene: Coleman and Bell C. P. grade was dried over sodium and recrystallized, f. p. 5.4°, n^{20}D 1.5007.

Toluene: Merck reagent grade, d^{20}_4 0.8667, n^{20}D 1.4968.

Anisole: Eastman grade, d^{20}_4 0.9950, n^{20}D 1.5172.

Diethyl Carbonate: Eastman grade, d^{20}_4 0.9750, n^{20}D 1.3850.

Isoamyl Chloride: Eastman grade, d^{20}_4 0.8927, n^{20}D 1.4096.

Water: Redistilled from alkaline permanganate through a block tin condenser and collected while hot.

Apparatus.—A modified "Cenco Film Pressure Apparatus" was used in these investigations. The aluminum tray and aluminum barriers were coated with Bakelite lacquer as described by McBain and Perry.[7] To maintain an unwettable surface on the tray at all times it was found desirable to apply a fresh coat of lacquer when any indications became evident of slight leakage between the barrier and edges of the tray. With constant usage this treatment was necessary only about once a month.

The mica float and platinum leaves of the balance were replaced several times during these studies but with the same steel torsion wire the calibrations always checked within ±1%. Six such calibrations gave an average conversion factor of 0.302±0.003 dyne per centimeter per degree of rotation on the scale.

An automatic micro-volume pipet like that suggested by Blodgett to Harkins and Anderson[8] was used for adding the benzene solution of unimolecular film material to the water surface in order that areas per molecule could be computed when desired.

Experimental

A unimolecular film was put on the water by means of a solution of the desired film material in benzene, and using the movable barrier the film was slightly compressed. A drop of liquid, benzene for example, was put on the film. It spread, pushed back the unimolecular film, and increased the pressure reading of the balance. The benzene drop

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[1] Samuel Avery Research Fellow, 1939–1940.

[2] Lord Rayleigh, *Proc. Roy. Soc.* (London), **A47**, 364 (1890).

[3] Harkins and Feldman, THIS JOURNAL, **44**, 2665 (1922).

[4] Cary and Rideal, *Proc. Roy. Soc.* (London), **109A**, 301 (1925).

[5] Blodgett, THIS JOURNAL, **57**, 1007 (1935).

[6] Langmuir and Schaefer, *Chem. Rev.*, **24**, 181 (1939).

[7] McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939).

[8] Harkins and Anderson, THIS JOURNAL, **59**, 2189 (1937).

TABLE I

MAXIMUM INCREASE OF FILM PRESSURE AS DROPS OF BENZENE ADDED

Palmitic Acid Film			Tristearin Film		
(1) Area per molecule, sq. Å.	(2) Initial pressure, dynes/cm.	(3) Pressure immediately after drop add.	(4) Area per molecule, sq. Å.	(5) Initial pressure, dynes/cm.	(6) Pressure immediately after drop add.
24.9	0.1	1.0	86.1	0.0	0.8
24.5	.2	1.5	83.4	.1	1.4
24.1	.2	1.8	80.8	.2	2.1
23.5	.2	3.6	78.0	.4	3.1
23.4	.3	4.8	75.1	1.0	5.1
23.2	3.9	8.2	73.8	1.3	5.8
23.1	6.4	8.8	72.3	2.2	7.1
23.0	7.6	9.4	71.0	3.1	8.2
22.9	8.8	9.5	69.5	5.6	9.4
22.8	9.6	9.6	68.1	9.5	9.5
22.7	10.8	10.8	66.9	13.2	13.2

evaporated in a few seconds and the balance returned to its original reading. As drops of benzene were added, at increased film pressures, the spreading decreased, and a series of film pressures were reached where the increased balance readings, with each added drop, showed practically the same value. By means of these values the spreading forces of various drop materials were measured. The only pressure entering was that due to the spreading of the drop material as a film. When this increased balance reading was normally due to the unimolecular film itself, no spreading of the benzene took place as a drop was added and there was no immediate change of film pressure.

The results of such an experiment with benzene and films of palmitic acid and tristearin are shown in Table I. Columns (1) and (4) contain the calculated area per molecule of the film material just before the addition of each drop of benzene. Columns (2) and (5) contain the balance reading just before the addition of each drop, while the readings that were reached immediately after the additions are listed in Columns (3) and (6).

The word "immediately" is used in Columns (3) and (6) in Table I for it was observed that further changes in pressure occurred during the existence of the spreading material as a lens. At film pressures just above that where no spreading occurred, as indicated by no immediate change in film pressure, a very small increase—fraction of a dyne—in pressure occurred during the life of the lens. At still higher film pressures, decreases during the evaporation of the lens were observed. These changes of pressure during the life of the lens should not be confused with the determination of the pressure exerted by the spreading material as a film.

The pressure which will just retain the added liquid as a visible lens, is very slightly higher than the pressure which best indicates the tendency of the liquid to spread as a film. When the spreading material existed as a small spherical lens, due to the restraining force of the unimolecular film, gravitational effects were probably introduced and the balance reading was very slightly greater than the pressure exerted by the spreading material as a film.

If the spreading material was exerting its maximum spreading pressure as a film, moving the barrier a few centimeters or adding more spreading material did not alter the balance reading until, because of the increased pressure, the added material assumed the lens form. This indicates a state of equilibrium between the spreading pressure of the liquid film and the pressure of the unimolecular film. Thus 9.5 would be chosen from Column (3) rather than 9.6, and 9.4 from Column (6) rather than 9.5 as the best measurement of spreading pressure.

The molecular area at which the maximum increase of pressure resulted from the addition of benzene on the tristearin film is practically three times the corresponding molecular area for palmitic acid. The molecular area at which no spreading takes place when benzene is added on a film of tristearin is about three times the corresponding molecular area for palmitic acid. This is interesting because the molecular area of a tristearin unimolecular film at zero compression is 61.5 sq. Å. (20.5 sq. Å. per chain) and the molecular area of a palmitic acid unimolecular film at zero compression is 20.5 sq. Å.

A summary of spreading pressure values for some of the liquids studied is recorded in Table II.

The results obtained with films of palmitic and stearic acids are practically the same. A film of tristearin did not give results with all spreading materials as readily. It has been suggested that this is because the film is so rigid that often there is not complete equalization of pressure over the surface.

TABLE II

SOME REPRESENTATIVE SPREADING PRESSURE VALUES

Unimolecular film	Spreading material	Spreading pressure, dynes/cm.	Harkins' spreading coefficients,[3] dynes/cm.
Palmitic acid	Nitrobenzene	3.6	3.76
Stearic acid		3.7	
Tristearin		3.6	
Palmitic acid	Toluene	8.7	6.84
Stearic acid		8.5	
Tristearin		8.4	
Palmitic acid	Benzene	9.5	8.94
Stearic acid		9.4	
Tristearin		9.4	
Palmitic acid	Anisole	11.6	11.76
Stearic acid		11.7	
Tristearin		11.3	
Palmitic acid	Diethyl carbonate	32.7	33.63
Stearic acid		32.7	
Tristearin		32.3	
Palmitic acid	Isoamyl chloride	14.6	33.88
Stearic acid		15.8	
Tristearin		..	

These values were obtained at temperatures between 20 and 25°. Within this range there was no noticeable change of spreading pressures with temperature.

Whereas the determination of spreading coefficients by Harkins' method requires three measurements of interfacial tension, in which four measurements of density are involved, this method requires only one measurement which is quickly carried out with a film pressure balance and a very small quantity of spreading material.

While the precision of a single reading is of the order of ±0.02 dyne/cm., the accuracy of the spreading pressures as indicated by the reproducibility of results is probably not greater than ±0.1 dyne/cm.

There are probably two principal sources of error:

1. The unimolecular film when under pressure can probably dissolve into the drop of the spreading liquid and thereby cause a decrease in area and a decrease in the observed pressure. This is possibly the explanation of the low values obtained with isoamyl chloride.
2. Vapors from the drop of applied liquid may be adsorbed into the film of stearic acid and cause it to expand so as to exert an abnormally high pressure.

Studies are now in progress on the accuracy of the determination of the spreading pressures of other pure organic liquids as well as on the behavior of binary mixtures of various compositions.

Summary

A method has been developed for the measurement of spreading pressures by means of a film pressure balance and a small quantity of the spreading liquid put on a unimolecular film.

Spreading pressures of nitrobenzene, toluene, benzene, anisole, diethyl carbonate, and isoamyl chloride on unimolecular films of palmitic acid, stearic acid, and tristearin have been measured by this method.

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The Equilibrium Composition of *n*-Butylmagnesium Chloride Solutions in Ethyl Ether

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It is well-known that solutions of Grignard reagents prepared from alkyl chlorides will deposit magnesium chloride on standing.[1] This presumably is due to the insolubility of the magnesium chloride etherate in ether and the existence of equilibrium 1.

$$\mathrm{RMgX} \rightleftarrows \mathrm{R_2Mg} + \mathrm{MgX_2} \qquad (1)$$

No quantitative determination of the solubility of anhydrous magnesium chloride in ether appears to have been reported but we have found it to be approximately 0.001 mole per 1000 g. of solution. With this marked insolubility one might predict that equilibrium 1 would be shifted completely to the right and that only dialkylmagnesium would remain in solution. That the magnesium chloride does not precipitate immediately was explained by Schlenk and Schlenk as due to the formation of metastable supersaturated solutions.

The work which we wish to report shows that in the case of Grignard solutions prepared from *n*-butyl chloride in ethyl ether, magnesium chloride does not completely precipitate under conditions

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[1] Schlenk and Schlenk, Jr., *Ber.*, **62**, 920 (1929); Cope, THIS JOURNAL, **57**, 2238 (1935).