who found that both human and bovine fibrinogen molecules are rod-like, filamentous structures.

On the basis of the data listed in Table I, there does not appear to be too great a difference in the size and shape of bovine and human fibrinogen. The discussion of other similarities or differences for these two proteins is beyond the scope of this paper.

The authors wish to thank Dr. F. Bueche for helpful discussions in connection with the light scattering results.

ITHACA, NEW YORK RECEIVED JUNE 7, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

# Wetting Characteristics of Cellulose Derivatives. I. Contact Angles Formed by Water and by Organic Liquids[1]

BY F. E. BARTELL AND B. ROGER RAY[2]

The wetting characteristics of each of a fairly extensive series of cellulose derivatives were determined by measuring the angle of contact of water and of various organic liquids against these derivatives. Fibers, rods, foils, films and coatings of the derivatives were used. A regular and systematic increase in the hydrophobic nature of the fatty acid esters was found to occur with increase in length of hydrocarbon chain; also, with the acetate derivatives, increase occurred with increase in acetyl content. Qualitatively, the increase in hydrophobicity with substituent groups was in the order: hydroxyl, formyl, acetyl, hydrogen phthalate, ethoxy, nitro, propionyl and benzoyl. The degree of polymerization appeared to have little influence on the wetting characteristics of the two sides. Organic liquids of high surface tensions tended to give finite angles of contact on the derivatives. Hysteresis of contact angle ranged from approximately 10° to over 40°. When cosines of the contact angles of water on a series of the fatty acid triesters were plotted against either the tensile strengths or the densities of the respective esters, a linear relationship was observed.

Soft solids such as cellulose derivatives and other polymers and resins, characterized as they are by low free surface energies, provide especially desirable surfaces for wettability investigation. Complications due to adsorption are at a minimum, and a number of liquids can be found which give finite and measurable values for both advancing and receding angles. These measured angles appear to be stable and closely reproducible. The available data on the wettability of cellulose derivatives, however, are limited to a few water–air–solid contact angle values, most of which are unreliable or ill defined. Some investigators have chosen to ignore the phenomenon of hysteresis of contact angle when making measurements on cellulose derivatives. Others have attempted to circumvent its effects. The hysteresis effect, *i.e.*, the difference between the angle formed when a liquid has been caused to advance over the solid and the angle formed when the liquid has been caused to recede, may be absent or negligible in some systems, but in most systems it is appreciable, and in the case of the cellulose derivatives it must be taken into account.

The specific objectives of the present research were to measure both the advancing and receding contact angles of water and of several organic liquids on representative cellulose derivatives and to correlate the data with the physical and chemical structures of these solids.

## Experimental Details

**Methods Used.**—The angles were measured by the vertical-rod, the tilting plate, or the controlled-drop-volume method (a modification of the usual drop-on-plate method) depending upon the nature of the solids to be studied. Numerous comparisons showed complete agreement among these methods.

In the vertical-rod method[3] either a fiber of the polymer, or a rod or a plate coated with a film of it, or a foil[4] was partially immersed in the liquid. A magnified silhouette of the liquid–solid interface was projected onto a screen or a photographic plate from which the angle could be measured directly. In the well-known tilting-plate method[5,6] the plate or rod was tilted until the liquid interface on one side remained perfectly horizontal up to the liquid–solid contact point. The angle of tilt gave the contact angle. In the controlled-drop-volume (or sessile drop) method[7,8] the angle was determined either by erecting a tangent upon the enlarged image of the drop or by calculations involving drop shape factors.

The vertical-rod and controlled-drop-volume methods proved to be superior because of the ease with which they enabled enclosure of the system so as to prevent vaporization, the convenience of observation of time effects, the facility with which advancing and receding conditions could be attained, and the accuracy possible over the entire range of 0 to 180°.

An air thermostat regulated to 25 ± 0.1° enclosed the contact angle device and cell and was supported independently so as to introduce no vibration. For vertical-rod (or vertical plate) and tilting-plate measurements a special supporting device and sample holder utilizing fine rack-and-pinion elements, made possible a sensitive and regular movement of the sample in the horizontal and vertical planes and also permitted a rotating movement about a fixed point which could be so adjusted that the center of rotation of the sample remained exactly at the interface of the liquid. Magnifications of from 5 to 1000× were used.

The controlled-drop-volume method was found to be the most suitable for some measurements on foils or on films. A critical requirement of this method is the sensitive and positive control of the drop volume accomplished by use of a pipet with a very fine tip (approximately 0.02 mm. o.d.) from which the liquid is either forced out by air pressure to

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[1] The data in this paper were taken from a portion of a thesis of B. Roger Ray, submitted to the School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the Ph.D. degree, December, 1945.

[2] Minnesota Mining and Manufacturing Co. Fellow, 1943–1945.

[3] F. E. Bartell, J. L. Culbertson and M. A. Miller, *J. Phys. Chem.*, **40**, 881 (1936).

[4] The term "foil" is used throughout to designate a sheet-like material of considerable thickness and rigidity and without a supporting base. The term "film" is reserved for a very thin layer of material attached to a supporting base.

[5] F. M. Fowkes and W. D. Harkins, THIS JOURNAL, **62**, 3377 (1940).

[6] N. K. Adam and H. L. Shute, *J. Soc. Dyers and Col.*, **53**, 121 (1937).

[7] F. E. Bartell and P. H. Cardwell, THIS JOURNAL, **64**, 494 (1942).

[8] F. E. Bartell and K. E. Bristol, *J. Phys. Chem.*, **44**, 86 (1940).

increase the volume of the drop in forming an advancing angle or sucked back in when forming a receding angle.

**Measurement of Contact Angles.**—For all the systems which gave finite and measurable angles, both stable advancing and stable receding angles were found. Initial angles quickly reached stable values which were sensibly constant with time up to periods of at least several hours (except for a few cases, so noted, in which the derivatives were partially soluble or highly swollen by the organic liquids). The angles were read at least three times over a period of 10 to 30 minutes in order to check the constancy; many systems were observed for a number of hours. Extended aging studies were made on several derivatives, and here, presumably because of sorption effects, the contact angles of water were, in some cases, found to change very slowly over a period of days.

Measurements on different regions of the same sample showed an average deviation of not more than ±1° for the individual measurements, while measurements on different samples of the same material showed an average deviation of not more than ±2°. No differences could be detected between the original angles and re-advancing and re-receding angles. Receding angles were ordinarily measured after a two-minute immersion, but the angles were the same after a two-hour immersion except when swelling was pronounced.

The contact angles did not appear to be significantly affected, within the limits of accuracy of the measurements, by prior conditioning of the solids, *i.e.*, exposing them to air or to vapors of the various liquids. The same values were found for the contact angles on freshly prepared surfaces of the derivatives as for these same surfaces after exposure to the air of the laboratory for more than two years. In general, the cellulose derivatives investigated behaved as soft inert solids with very reproducible surfaces and appeared to be free of significant adsorptive effects.

**Materials.**—The best available grades of organic liquids were further purified until free of all traces of surface-active contaminants as shown by the values for the surface tensions and also for the interfacial tensions of the liquids against water. Since one objective of the research was to interrelate the data of the three separate contact angle systems on each solid[9] organic liquids saturated with water were used throughout, inasmuch as the surface tensions of the water-saturated liquids are not appreciably different from those of the pure liquids and there appeared to be no adsorption effects.

The organic liquids of highest surface and interfacial tensions (and only these gave finite angles on the derivatives) affect the surface tension of water but little. No differences that exceeded the experimental errors of the measurements were found between the angle values given by the high surface tension organic liquids when pure and those given by the liquids when saturated with water. The same was true for water, pure or saturated with organic liquid. Such agreement is not to be expected, however, if these liquids are used with a different type of solid, *i.e.*, certain hard solids.

Some of the cellulose derivatives examined were supplied by manufacturers and consisted of representative commercial products stated to be of high purity and to be free of other substances.[10] A number of the derivatives were from batches prepared and purified in connection with other research projects and were supplied through the courtesy of the investigators.[11] The remainder of the derivatives were prepared in this Laboratory using a modified Clarke and Malm procedure.[12,13] The reactions took place smoothly at relatively low temperatures and, with the exception of the tripalmitate, with no darkening of the products.[14] After several reprecipitations and washings the products were analyzed.[15]

## Experimental Results

In Table I are given the values of the water–air–solid angles of contact on films of the cellulose acetates comprising Series 1. The films were cast on glass rods from a 10% solution of either acetone–ethanol or of chloroform. Evaporation took place slowly under controlled conditions of low humidity at room temperature. After 24 hours the coated rods were heated at 70° for three hours.

TABLE I

CONTACT ANGLES IN AIR OF WATER ON CELLULOSE ACETATES OF VARYING DEGREES OF SUBSTITUTION

| Series 1 No. | Extent of acetylation, % | Advancing contact angle, degrees | Receding contact angle, degrees |
|---|---|---|---|
| 1 | 38.1 | 63.8 | 44.5 |
| 2 | 38.6 | 64.0 | 42.0 |
| 3 | 40.2 | 64.0 | 43.0 |
| 4 | 41.0 | 64.7 | 43.0 |
| 5 | 42.2 | 65.0 | 48.5 |
| 6 | 43.3 | 65.2 | 52.0 |
| 7 | 44.5 | 68.3 | 56.0 |
| 8 | 45.0 | 68.5 | 52.0 |

Foils of the polymers were made by pouring solutions onto clean pieces of plate glass using narrow glass strips as barriers. After 24 to 48 hours of controlled evaporation the foils were heated at 70° for 60 hours and were then stripped from the glass plates. The cellulose acetates comprising the first ten samples in Table II were cast from 10% solutions of the solvents noted, whereas the remainder of the derivatives were cast from 20% solutions. Foils of the last four derivatives could not be completely removed from the glass because of their softness and adherency. This difficulty was experienced also with the fatty acid triesters above the propionate.

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(9) The present paper deals with the contact angles of water and of different organic liquids on the cellulose derivatives. A later paper will pertain to the interfacial contact angle systems and the relationship found among the three systems.

(10) These materials were received in the form of crumbs (cellulose acetates no. 60, 65, 50, 44, triacetate, acetopropionate-E, acetate hydrogen phthalate, acetate, stearate, nitrates H-1 and H-2, and ethyl cellulose-E) or as both crumbs and foils (acetate-FM2, acetopropionate-H, acetobutyrate-H and ethyl cellulose-H). Data supplied with these samples appear in Table II.

(11) Eight acetate samples, comprising Series 1, were supplied by Dr. W. A. Mosher formerly of Hercules Powder Company. These differed in acetyl content, as shown in Table I, but were uniform with respect to viscosity. Four acetate samples (Series 2), differing in viscosity but of uniform acetyl content, were supplied by Mr. Arnold Sookne, Textile Foundation, National Bureau of Standards. In Table II are given the data on these samples. They were representative fractions from a batch of highly purified acetate used by A. M. Sookne, H. A. Rutherford, H. Mark and M. Harris, *Bureau Standards J. Research*, **29**, 123 (1942), in fractionation studies. The original starting material was fractionally precipitated from acetone by the addition of ethanol and the degree of polymerization (D.P.) of each fraction determined viscometrically. The D.P. values are given in terms of the number of glucose residues per average chain length. Four fatty acid triesters (propionate, caproate, heptoate and laurate) were supplied by Dr. S. E. Sheppard, Eastman Kodak Company. They were portions of the batches prepared by S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **39**, 143 (1935).

(12) Hans T. Clarke and Carl J. Malm, U. S. Patent 1,880,808 (October 4, 1932).

(13) German Patent 516,250 and others; "Cellulose Verbindungen," Ed. by O. Faust, pp. 1327–1335, Vol. I, Edwards Bros., Ann Arbor, Mich., 1943 (reprint).

(14) Although both primary and regenerated cellulose were used as starting materials, it was found advantageous to use regenerated cellulose obtained by deacetylation of cellulose acetate for our preparations since this more reactive form gave rapid and uniform reactions. The amount of moisture within the cellulose seemed to be of great importance. Cellulose dried at 100° or even thoroughly air dried, reacted superficially. Complete solution could only be obtained by raising the temperature so high that some darkening took place.

(15) The modified Eberstadt method of C. J. Malm, Leo B. Genung, Robert F. Williams, Jr., and Mary A. Pile, *Ind. Eng. Chem. Anal. Ed.*, **16**, 501 (1944), was used except for the formate which was analyzed by total oxidation in standard potassium dichromate–sulfuric acid reagent. The analyses of the former varied between 2.5 and 3.0 in degree of substitution while a value of 1.9 was found for the formate.

TABLE II

CONTACT ANGLES IN AIR OF WATER ON THE OPPOSITE SURFACES OF FOILS OF CELLULOSE DERIVATIVES

| | | Contact angle "air" side | | | Contact angle "glass" side | | | Difference in angle on the two sides | |
|---|---|---|---|---|---|---|---|---|---|
| Cellulose derivative | Solvent[a] | $\theta^a$ degrees | $\theta^r$ degrees | $\Delta\theta$ degrees | $\theta^{a\prime}$ degrees | $\theta^{r\prime}$ degrees | $\Delta\theta'$ degrees | $\theta^a - \theta^{a\prime}$ degrees | $\theta^r - \theta^{r\prime}$ degrees |
| Series 2. Cellulose acetate fractionated as to degree of polymerization (D.P.) | | | | | | | | | |
| Original: 38.6% acetyl, D.P. = 194 | a | 64 | 41 | 23 | 67 | 30 | 37 | −3 | 11 |
| Fraction 3: 38.5% acetyl, D.P. = 345 | a | 62 | 39 | 23 | 70 | 31 | 39 | −8 | 8 |
| Fraction 8: 38.5% acetyl, D.P. = 194 | a | 61 | 45 | 16 | 69 | 37 | 32 | −8 | 8 |
| Fraction 14: 39.0% acetyl, D.P. = 68 | a | 65 | 42 | 23 | 75 | 33 | 42 | −10 | 9 |
| Representative cellulose acetates of commercial origin | | | | | | | | | |
| No. 60: 38% acetyl, high visc. type | b | 64 | 44 | 20 | 68 | 23 | 45 | −4 | 21 |
| No. 55: 38% acetyl, medium visc. type | b | 64 | 46 | 18 | 65 | 26 | 39 | −1 | 20 |
| No. FM2: 40% acetyl, medium visc. type | b | 64 | 42 | 22 | 62 | 25 | 37 | 2 | 17 |
| No. 50: 42% acetyl, medium visc. type | b | 65 | 52 | 13 | 60 | 23 | 37 | 5 | 29 |
| No. 44: 42% acetyl, low visc. type | b | 67 | 51 | 16 | 68 | 26 | 42 | −1 | 25 |
| Triacetate: 45% acetyl, medium visc. type | c | 69 | 52 | 17 | 63 | 27 | 36 | 6 | 25 |
| Other cellulose derivatives | | | | | | | | | |
| Acetopropionate-E: 16% propionyl | b | 69 | 48 | 21 | 70 | 34 | 36 | −1 | 14 |
| Acetopropionate-H: 31% propionyl | d | 75 | 53 | 22 | 73 | 34 | 39 | 2 | 19 |
| Tripropionate | c | 79 | 70 | 9 | 78 | 64 | 14 | 1 | 6 |
| Acetobutyate-H: 20% butyryl | e | 73 | 54 | 19 | 71 | 45 | 26 | 2 | 9 |
| Acetate hydrogen phthalate | b | 68 | 49 | 19 | 56 | 28 | 28 | 12 | 21 |
| Acetate stearate | b | 92 | 51 | 41 | 92 | 46 | 46 | 0 | 5 |
| Ethyl cellulose-H: 47% ethoxy | b | 76 | 45 | 31 | 76 | 45 | 31 | 0 | 0 |
| Ethyl cellulose-D: 49% ethoxy | b | 75 | 45 | 30 | 75 | 44 | 31 | 0 | 1 |
| Nitrate-H-1: 11% nitrogen | b | 77 | 47 | 30 | 64 | 23 | 41 | 13 | 24 |
| Nitrate-H-2: 12% nitrogen | b | 75 | 46 | 29 | 68 | 25 | 43 | 7 | 21 |
| Benzoate[b] | c | 79 | 61 | 18 | | | | | |
| Ortho-chlorobenzoate[b] | c | 76 | 68 | 8 | | | | | |
| Cinnamate[b] | c | 79 | 63 | 16 | | | | | |
| Phenylacetate[b] | c | 82 | 70 | 12 | | | | | |

[a] The foils were cast from the following solvents: (a) acetone, (b) acetone–ethanol–chloroform, (c) chloroform, (d) ethyl acetate–butyl acetate (e) ethylene dichloride–butanol–butyl acetate. [b] Foils of these derivatives could not be stripped cleanly from the glass.

In most cases the contact angles on the two sides of a foil cast on glass (or metal) differed significantly. The values were closely reproducible on duplicate foils, presumably due in part to the standardized conditions under which the foils were made. The advancing and receding contact angle values, $\theta^a$ and $\theta^r$, for water on these foils are summarized in Table II.

Uniform films of the cellulose triesters of most of the fatty acids from formic through stearic were coated onto glass rods from 10% chloroform solutions using the same technique as for Series 1 above. The diformate was soluble only in formic acid and was cast from this solvent. Contact angle results for water and for several organic liquids against these coated rods in air are given in Table III.

Only a few organic liquids were found which would give finite and measurable advancing and receding contact angles on the derivatives without appreciably softening or dissolving them. In general, these angles quickly reached stable reproducible values characteristic for each surface. The satisfactory liquids all had high surface tensions and high interfacial tensions against water; those having lower surface and interfacial tensions completely wet the solids giving zero angles.

The tendency of the derivatives to dissolve, at least partially, in the organic liquids prevented measurements on the higher fatty-acid esters. For some of the lower fatty-acid esters, as well as for other derivatives, certain of the organic liquids gave limited swelling and softening. In these cases the initial angles usually changed more or less slowly and reached stable, finite values. These systems are shown in Table III with parentheses around the approximate initial values and arrows indicating the final and apparently stable values. In some cases the swelling was slight and the initial angles did not change appreciably with time; these values are enclosed in parentheses.

The last four derivatives in Table III were those which showed minimum swelling and solubility effects. Each foil had been produced on commercial equipment by flowing a 20% solution onto a large metal roll and evaporating the mixed solvent.[16] For comparison with these commercially made foils a film of acetate FM2 was made in this Laboratory from 20% acetone–ethanol–chloroform.

## Discussion of Results

**Effects of Substituent Groups.**—It will be noted that the contact angles found for the different derivatives vary over a wide range of values and that pronounced hysteresis effects exist.

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(16) These solvents were: acetone–methanol for the acetate, ethyl acetate–butyl acetate for the acetopropionate, ethanol–ethylene dichloride for the acetobutyrate, and toluene–ethanol in the case of the ethyl cellulose.

TABLE III

CONTACT ANGLES IN AIR OF SEVERAL LIQUIDS ON SURFACES OF CELLULOSE DERIVATIVES

| Series 3 Cellulose derivatives | Water $\theta^a$ degrees | Water $\theta^r$ degrees | Methylene iodide $\theta^a$ degrees | Methylene iodide $\theta^r$ degrees | Acetylene tetrabromide $\theta^a$ degrees | Acetylene tetrabromide $\theta^r$ degrees | $\alpha$-Bromonaphthalene $\theta^a$ degrees | $\alpha$-Bromonaphthalene $\theta^r$ degrees | Bromobenzene $\theta^a$ degrees | Bromobenzene $\theta^r$ degrees |
|---|---|---|---|---|---|---|---|---|---|---|
| Diformate, film | 54.5 | 10 | | | | | | | | |
| Triacetate, film | 67.5 | 52 | 47 | 39.5 | (33) | (0) | 33.5 | 24 | 7 | 0 |
| Tripropionate, film | 79 | 69.5 | 65 | 41.5 | (42→0) | (0) | (46) | (0) | (47→0) | (0) |
| Tributyrate, film | 87 | 74 | 60 | 37.5 | (75→0) | (0) | | | | |
| Trivalerate, film | 92 | 74.5 | (90→56) | (34) | | | | | | |
| Tricaproate, film | 100 | 75.5 | ( →53) | (33) | | | | | | |
| Triheptoate, film | 104.5 | 76.5 | | | | | | | | |
| Tricaprylate, film | 105.5 | 77 | (90→44) | (26) | | | | | | |
| Trilaurate, film | 107 | 83 | | | | | | | | |
| Tripalmitate, film | 103 | 86.5 | | | | | | | | |
| Tristearate, film | 108.5 | 89 | | | | | | | | |
| Acetate FM2 | | | | | | | | | | |
| (a) Foil, side A[a] | 64 | 40 | 40 | 18 | (10) | (0) | 28 | 6 | 11 | 0 |
| (b) Foil, side B[b] | 61 | 30 | 42 | 20 | (11) | (0) | 28 | 6 | 12.5 | 0 |
| (c) Film | 64 | 42 | 44 | 33 | | | | | | |
| Acetopropionate H | | | | | | | | | | |
| (a) Foil, side A[a] | 74 | 53 | 49 | 31 | (19→0) | (16→0) | 34 | 20 | 17 | 0 |
| (b) Foil, side B[b] | 72 | 40 | 46 | 25 | | | 28 | 6 | 8 | 0 |
| Acetobutyrate H | | | | | | | | | | |
| (a) Foil, side A[a] | 76 | 53.5 | 46 | 21 | (17) | (0) | 32 | 8 | 13 | 0 |
| (b) Foil, side B[b] | 75.5 | 48.5 | 43 | 17 | (18) | (0) | 23.5 | 11 | 14 | 0 |
| Ethyl cellulose H | | | | | | | | | | |
| (a) Foil, side A[a] | 80 | 47 | 57 | 37 | (50) | (0) | (46) | (0) | (30.5) | (0) |
| (b) Foil, side B[b] | 74 | 44 | 59 | 30 | (56) | (0) | (49) | (0) | (29.5) | (0) |

[a] Side A formed in contact with air. [b] Side B formed in contact with metal.

It appears that the major determining factors are, first, the nature and number of groups substituted into the polymer chain and, second, the mode of formation of the surface of the polymer.

Other work in this Laboratory has shown that pure cellulose, from whatever source, is completely wet by water. Cellulose diformate, the most hydrophilic derivative examined in the present research, has an advancing angle of 54.5°, indicating that a substantial decrease in attraction of water is produced by the substitution of formyl groups for two of the hydroxyl groups of the pyranose ring. A regular and systematic decrease in hydrophilic character of the derivatives occurs as the length of the hydrocarbon chain is increased, as shown by column 2 in Table III. Cellulose tristearate, with an angle of 108.5°, is wetted by water to about the same degree as is paraffin.

From among the last group of derivatives listed in Table II a comparison can be made of the effects of fatty acid side chains when present in different proportions in mixed esters. Acetopropionate-E, 16% propionyl content, has an advancing angle of 69° and sample H, 31% propionyl, has an angle of 75°; whereas tripropionate has an angle of 79°. Acetobutyrate-H is seen to fall between the triacetate (Table III) and the tributyrate.

A qualitative arrangement can be made of the substituent groups in the various cellulose derivatives in the order of increasing contact angle with water, namely: hydroxyl, formyl, acetyl, hydrogen phthalyl, ethoxy, nitro, benzoyl, propionyl, phenylacetyl and butyryl. Approximately this same order is observed when the groups occur in simple organic molecules and are arranged in order of decreasing attraction for water as measured by the length of the hydrocarbon chain necessary to prevent solution of the molecule.[17] This general correlation between the angle of contact and the relative water-attracting tendency of each group indicates that the same secondary valence forces are operative. It is also good evidence that the surface layers of the solids have a similar mode of orientation which more or less fully exposes the substituent groups and permits them to influence strongly the wetting characteristics of the polymer.

**Effects of Degree of Substitution and of Polymerization.**—To evaluate the effects of degree of substitution and of polymerization on the contact angles of water, measurements were made on three series of cellulose acetates. Data on the first series, consisting of eight samples of the same average degree of polymerization but of different acetyl contents, are given in Table I and clearly show the small progressive increase of the angle with acetyl content. Angles measured on the "air" sides of foils of six additional representative cellulose acetates (Table II) show also that wettability is increased with acetyl content but is practically independent of viscosity.

The effect of degree of polymerization is shown by Series 2, Table II. The starting material, a cellulose acetate of 38.6% acetyl content and an average degree of polymerization of 194, was separated into fractions of different degrees of polymerization. The wetting characteristics of the different fractions are seen to be similar, most of the differ-

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[17] N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd Ed., Oxford University Press, London, 1941, p. 93.

ences being of the same order as the reliability of the measurements. It can be concluded that the degree of wetting of cellulose acetates is primarily a function of the composition and is little affected by variations in the degree of polymerization (within the practical range of use).

**Fatty Acid Triesters.**—In Fig. 1 the contact angles of water on these esters are plotted against the number of carbon atoms in the ester group.

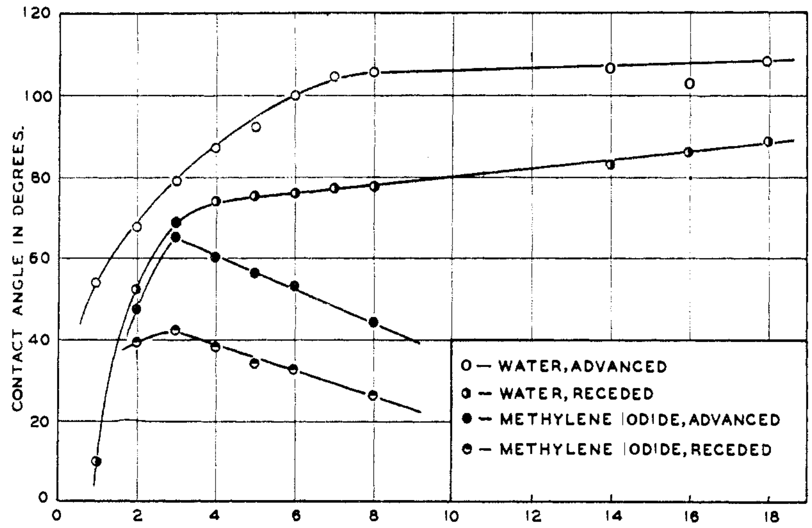

Fig. 1.—Contact angles of esters plotted against number of carbon atoms.

Shown also are the angles of methylene iodide on the lower members of the series. The advancing angles of water on the valerate and palmitate seem low, but new preparations, carefully purified. gave the same values. A sample of propionate made in this Laboratory and one prepared in another laboratory gave values which were in complete agreement.

The regular progression of the angles on the fatty acid esters as shown in Fig. 1 points to an incomplete but fairly uniform orientation of the surface molecules. Complete orientation, such as in certain monomolecular films, would be expected to give either very high or very low wetting. On the other hand, there is good evidence from X-ray and monolayer spreading measurements that films of these esters exhibit crystallinity and have characteristic modes of orientation.

When the cosines of the contact angles of water on the triesters are plotted against either the tensile strengths or the densities of the respective esters a linear relationship is found as shown in Fig. 2. The tensile strength and density data are from Sheppard and Newsome.[11] Although tensile strength is dependent upon the degree of polymerization, the contact angle is apparently much less dependent upon it. It therefore seems permissible to compare the tensile strength data obtained on a series of triesters, prepared from the same source and in a uniform manner, with the contact angle data obtained in this research.

The progressive decrease in tensile strength results from progressively weaker intermolecular binding forces. The densities of organic compounds also are, to a first approximation, determined by these forces. The degree of wetting of a solid is governed by the balance of the intermolecular attractive forces operative at the air–solid and water–solid interfaces, specifically, it is the cosine of the angle of contact that is significant in the expression which equates these forces. It is not surprising, therefore, to find approximate linear relationships among these three physical properties.

**Contact Angles Formed by Organic Liquids.**—From Table III it can be seen that finite and measurable values were given by methylene iodide in all cases. (Heptane, toluene, carbon tetrachloride and benzene wet completely all the polymers.) Limited swelling of some of the polymers in the liquids was observed (denoted by parentheses) but did not preclude the formation of stable, reproducible values. For the lower member of the series the angles increase with increase in length of the hydrocarbon side chains present in the polymer, but with the tripropionate a reversal occurs and the angles progressively decrease for successive higher members. In the ideal case, which neglects hysteresis and possible other effects, the expression for the balance of forces at an interface of air, liquid and solid is given by the Young[18] equation

$$S_{la} \times \cos\theta + S_{sl} = S_{sa}$$

where the subscript 1, a and s stand for liquid, air and solid, respectively, and $S$ stands for surface or interfacial tension of an interface. In terms of this

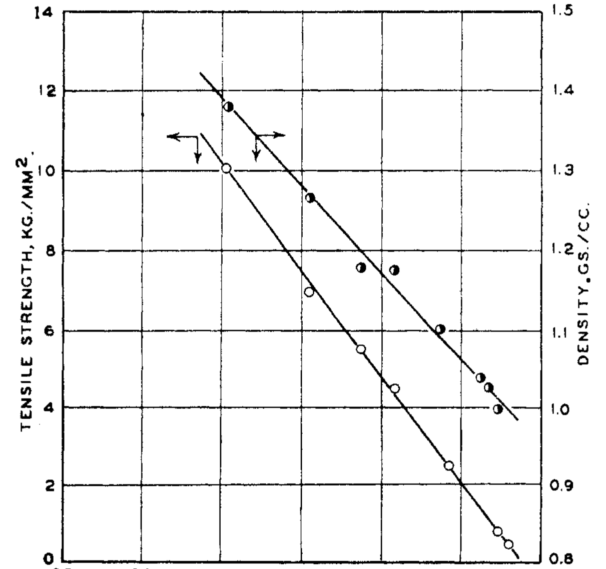

Fig. 2.—Cosines of contact angles of water on a series of triesters plotted against tensile strengths and densities of the respective esters.

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[18] T. Young, *Phil. Trans.*, 65 (1805).

equation it appears that, initially, the surface tension of the solid, $S_{sa}$, decreases more in passing from one derivative to the next higher one than does the interfacial tension solid–liquid, $S_{sl}$, but that beyond the maximum point the reverse is true. This explanation agrees with other facts, *i.e.*, that the tensile strength and density (to a first approximation proportional to $S_{sa}$) decrease throughout quite linearly with increasing side chain length, whereas solubility and swelling effects (inversely related to $S_{sl}$) become much more pronounced starting with the tributyrate.

**Hysteresis Effects.**—As can be seen from the tables differences between the advancing and receding angles, for the liquid–solid combinations which give finite angles, ranged from 8° to over 50°. In each case the amount of the hysteresis appears to be characterisitc of the derivative and of the mode of formation of the surfaces.

The organic liquids gave hysteresis effects which on some solids exceeded those given by water. There is some indication, at least for methylene iodide, that the effects with organic liquids are the inverse of those with water. As shown in Fig. 1 the hysteresis with methylene iodide becomes a maximum at the tripropionate, whereas that with water is a minimum.

That the magnitude of the hysteresis effect is dependent upon the mode of formation of the surface is clearly shown in Table II upon comparing $\Delta\theta$ values for the opposite sides of foils. The higher values are for the "glass" sides where the average value is nearly double that found for the "air" sides. As brought out in the last two columns of the table these differences in hysteresis are for the most part the result of differences in the receding angles on the opposite sides. The majority of the receding angles are around 20° lower on the "glass" sides than on the "air" sides while the advancing angles differ little or none on the two sides. Ethyl cellulose furnishes the exception to the above generalization. With it the contact angles and hysteresis were the same for the two sides of the foil. A possible explanation for the smaller receding angle on the "glass" side is that molecular orientation occurred in the surface of the cellulose derivative against the hydrophilic glass which caused this surface of the polymer to become more hydrophilic.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 7, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

# Photochemical Studies. XLV. The Reactions of Methyl and Acetyl Radicals with Oxygen[1]

BY FRANK B. MARCOTTE AND W. ALBERT NOYES, JR.

Acetyl radicals apparently do not yield either carbon monoxide or carbon dioxide upon reaction with oxygen although it appears that two molecules of oxygen are consumed per radical. It is possible to obtain a rough estimate for the activation energy of the reaction $CH_3CO = CH_3 + CO$ if it is assumed that the activation energy for reaction of acetyl radical with oxygen is very small. Previous work has been extended to give some further information about the formyl radical.

Some results obtained during exposure of mixtures of acetone and oxygen, the latter at quite low pressures, have already been presented.[2] Due to the fact that the quantum yields of oxygen disappearance and of the sum of carbon monoxide and carbon dioxide formation were in general approximately small whole numbers, it was possible to present a relatively simple mechanism which accounted for most of the facts. Not many, if any, of the steps in this mechanism could be proved conclusively although no alternative mechanism of equal plausibility could be suggested. The present work is a continuation of that already reported and helps to elucidate certain of the steps.[3]

## Experimental

The experimental procedure used in this investigation has been described adequately.[2] Analyses were performed for methane, carbon monoxide, ethane and carbon dioxide, and values were also obtained for the amount of oxygen consumed during the course of the reaction. Methane, carbon monoxide and oxygen were separated from all other products as well as from the acetone by condensation with liquid nitrogen. Since ethane is not produced when oxygen is present, it proved unnecessary to use supercooled liquid nitrogen. The oxygen, carbon monoxide and methane were heated in a furnace containing a mixture of copper and copper oxide. The oxygen is removed as copper oxide, the carbon monoxide is oxidized to carbon dioxide, and the methane is not affected by this procedure.

Since the method of competing reactions was used, low pressures of oxygen were essential. In order to avoid its depletion, small amounts of oxygen were added from time to time by means of a small Toepler pump. The gases were circulated by a small glass propeller.

Quantum yields are based on a value of unity for the quantum yield of carbon monoxide formation in pure acetone vapor at temperatures between 120 and 225°.[4,5]

## Results

The important matters in the present discussion are the details of the variation of the yields of carbon monoxide, carbon dioxide, and oxygen disappearance as a function of oxygen pressure over the temperature range, 120 to 225°. Figure 1 shows carbon monoxide yield as a function of oxygen pressure at five different temperatures whereas Fig. 2 shows similar data for the carbon dioxide yield. Figure 3 shows the variation of methane yield.

It is evident that the yield of carbon dioxide passes through a maximum as a function of oxygen pressure at the lower temperatures in this temperature range. It may do so

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[1] This work was supported in part by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

[2] F. B. Marcotte and W. A. Noyes, Jr., *Discussions Faraday Soc.*, No. 10 (1951).

[3] For detailed tables of data pertaining to this work order Document 3366 from American Documentation Institute, 1719 N Street N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1″ high on standard 35 mm. motion picture film) or $1.05 for photocopies (6″ × 8″) readable without optical aid.

[4] J. A. Leermakers, THIS JOURNAL, 56, 1899 (1934).

[5] D. S. Herr and W. A. Noyes, Jr., *ibid.*, 62, 2052 (1940).