Summary

1. α-Furfuryl chloride has been isolated in a pure state, analyzed and its physical properties have been determined. It is a relatively unstable substance but of sufficient stability to be distilled in a vacuum and used in a variety of reactions. It seems obviously more stable than the corresponding bromide and iodide. This is the first time the parent ω-halogen methyl furan has been obtained in a pure, free condition, having previously been known only in solution.

2. The chlorine atom possesses a high order of reactivity, comparable to that of the chlorine in benzyl chloride. Eight ethers have been prepared from the α-furfuryl chloride and their physical properties determined. The allyl-α-furfuryl ether has been prepared by the direct reaction between the chloride and allyl alcohol.

3. The synthesis of this reactive chloride has opened up new possibilities in the furan series and investigations of other reactions using α-furfuryl chloride are being continued.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

A METHOD FOR THE MEASUREMENT OF INTERFACIAL TENSION OF LIQUID-LIQUID SYSTEMS[1]

BY F. E. BARTELL[2] AND F. L. MILLER[3]

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Recently the authors were confronted with the problem of measuring the interfacial tension between water and a series of crude petroleum oils. Some of these oils were very dark, practically black; consequently, the methods most generally used for interfacial tension measurements were not satisfactory. With the more transparent oils the Reynolds capillary tube method[4] was used, but with the darker oils the liquid interface within the capillary could not be seen. After considerable experimentation a method was developed by means of which it was possible to determine the interfacial tension between the dark oils and water and subsequently it was found that this method gave results which checked well with what

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[1] This paper contains preliminary results obtained in an investigation on the "Displacement of Petroleum Oils from Oil Bearing Sands by Means of Selected Aqueous Solutions," listed as Project No. 27 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project 27.

[3] American Petroleum Institute Research Assistant.

[4] Reynolds, *Trans. Chem. Soc.*, **119**, 460–466 (1921).

we believe to be some of the most reliable values to be found in the literature. The apparatus is simple in construction, is easy to operate and measurements can be quickly carried out.

Ferguson[5] has presented discussions covering the different methods which have been used for interfacial tension measurements; accordingly, no comprehensive discussion will be presented in this paper. It is well known that the most generally used methods have involved either the principles of the drop weight or the capillary rise method. The capillary rise method has been used with modification by Lerch,[6] Clark,[7] Reynolds,[4] Harkins and Humphery[8] and others, and not always with agreement in results. It is believed that the results reported by Harkins and Humpherys represent about the most accurate values obtained to date with a method based upon capillary rise.

The result of our experience with a number of the existing methods led first to the construction of an exceptionally simple apparatus with which apparently very satisfactory results were obtained (Fig. 1). The apparatus consists of a glass cup, A, about 4 cm. in diameter and 8 cm. in depth to the bottom of which is sealed a capillary tube outlet of about 0.3mm. radius. The remainder of the apparatus consists only of an open dish, B, which is large enough to eliminate effects due to capillarity.

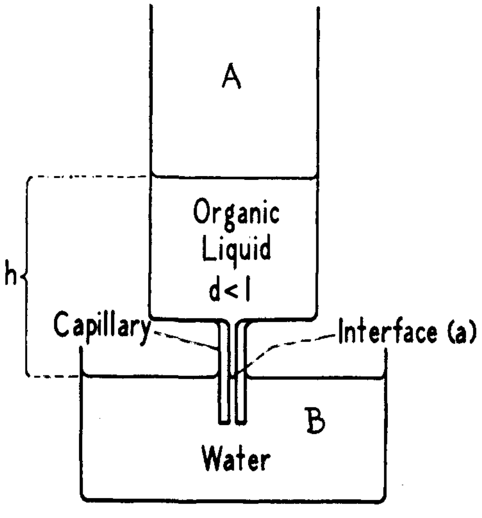

Fig. 1.

For the determination of interfacial tension, one immerses the capillary in the dish of water (B) until the calibration mark (a) is exactly level with the surface. Water will rise in the capillary to the bottom of the cup, thereby wetting the capillary throughout its length. The organic liquid (or oil) to be used is then slowly added from a buret, at the later stages drop by drop, until the water-organic-liquid interface is forced downward to the calibrated mark (a). The height of the organic liquid is then readily measured by means of a cathetometer. Knowing the density of the organic liquid, the interfacial tension, S_{23}, is calculated from the formulation

$$S_{23} = \frac{rhdg}{2} \qquad (1)$$

The results obtained with this apparatus for different organic liquids

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[5] Ferguson, Brit. Assn. Adv. Sci., *Fifth Report,* Colloid Chem., **1923,** pp. 1-13.

[6] Lerch, *Ann. Physik,* **9,** 434 (1902).

[7] Clark, *Proc. Amer. Acad.*, **41,** 361 (1906).

[8] Harkins and Humphery, THIS JOURNAL, **38,** 242 (1916).

against water showed close agreement with those obtained by Harkins and co-workers.[9]

The advantages of this apparatus are that it can be constructed from the materials to be found in almost any chemical laboratory and by one not expert in the art of glass blowing. The only precaution to be observed in construction is that excessive constriction or enlargement of the capillary at any point must be avoided; otherwise, difficulty will be encountered in bringing about a gradual descent of the liquid–liquid interface to the mark of calibration. Although this apparatus appeared to give good results, certain disadvantages were encountered such, for example, as the impracticability of using liquids denser than water, as also difficulty in obtaining exact temperature control.

A detailed description of this simple apparatus is given herewith, inasmuch as it is felt that this apparatus may prove to be well suited to the needs of some investigators and, further, it has been found to be satisfactory when placed in the hands of students in the regular laboratory courses.

An apparatus was next constructed which could be used with liquids of any density and which could be placed in a water thermostat and held at any desired temperature. In our experiments a thermostat with plane glass sides was used and readings were made through this glass.

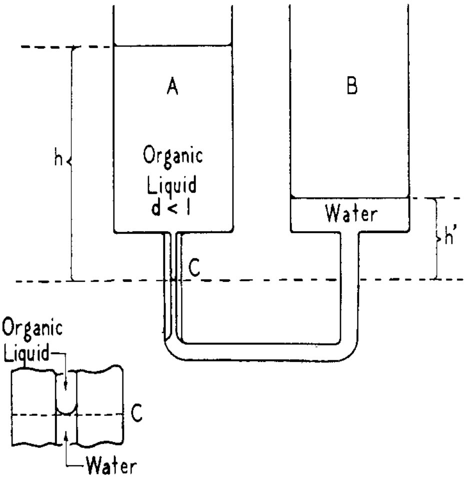

Fig. 2.

The apparatus is shown in Fig. 2. It consists of two cups, A and B about 4 cm. in diameter and 8 cm. in height. These are connected by glass tubing, one arm of which is a capillary tube of approximately 0.3-mm. radius. The operation of this apparatus is similar in principle to that previously described. In case the organic liquid to be used is less dense than water, the latter (about 10 cc. or more) is put into cup B. It will completely fill the glass tube and will mount to the top of the capillary tube. Immediately the organic liquid is introduced at A so that a liquid–liquid interface is formed at the upper end of the capillary. More liquid is added, finally drop by drop, until the interfacial meniscus is forced down even with the calibration mark at C. Readings h and h', the heights of the organic liquid and water, respectively, above this meniscus, are now taken by means of a cathetometer.

In case the organic liquid is denser than water, the operation is somewhat different. Water (about 10 cc.) is put into cup A until it mounts just to the top of the tube in the

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[9] Numerous papers on interfacial tension.

bottom of cup B (Fig. 3). The organic liquid (as chloroform, etc.) is now added slowly to cup B, so that the water is forced back until the liquid interface enters the lower end of the capillary and finally reaches the mark C. Readings are taken with the cathetometer as before.

In either of the above cases the procedure is simple and the time required for a determination is not over ten to fifteen minutes. The formulation used in this case is as follows

$$S_{23} = \frac{rg}{2}(hd-h'd') \qquad (2)$$

in which h and d are the height and density of the organic liquid and h' and d' are the height and density of water, respectively.

The radius of the capillaries in both types of apparatus is determined by suspending the inverted cup at a given temperature in a pure liquid (as benzene) of known surface tension (S for benzene is taken as 28.25) for this temperature (25°). By carefully adjusting the apparatus the meniscus is brought to the etched mark on the capillary. The height of this meniscus above the level of the liquid in the container is measured with a cathetometer. The radius, r, is thus determined from the formula

$$S = \frac{rhdg}{2} \qquad (3)$$

or

$$r = \frac{2S}{hdg} \qquad (4)$$

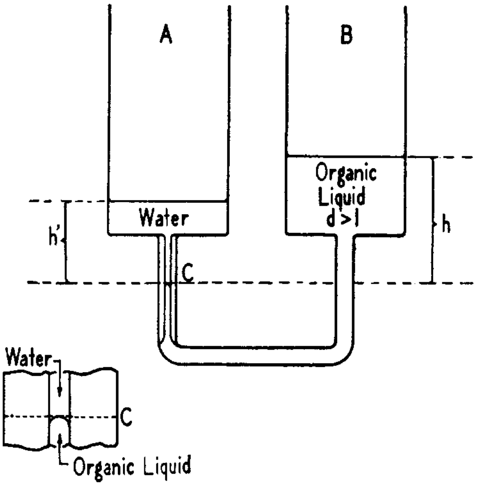

Fig. 3.

Meniscus Corrections.—In the determination of surface tension of a liquid by the capillary rise method, the height of the liquid is measured only to the lowest point of the meniscus. This leaves a small quantity of liquid above this point which should be considered and for which a correction in the reading should be made. In order to determine the height representative of the true mass of the liquid column supported by the force of surface tension, a correction must be added. The actual value in terms of height of liquid which should be considered in this correction is approximately one-third that of the height of the meniscus itself. Different investigators[10] have employed somewhat different meth-

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[10] Laplace, "Mécanique Celeste," Supp. au livre 10, **1805**; Poisson, "Nouvelle Theor. de l'Action Capill.," **1831**; Mathieu, "Théorie de la Capillarité," Ch. II, Ch. IV, **1883**; Lohnstein, *Wied. Ann.*, **54,** 713 (1895); Rayleigh, *Proc. Roy. Soc.*, **92A,** 184 (1915); Schrodinger, *Ann. Physik.*, **46,** 111, 413 (1915).

ods in making this correction. A generally accepted correction is that given by Poisson,[11] who expressed the correction as a function of the radius of the capillary. The equation follows (h_0 represents the observed height of the liquid column)

$$h = h_0 + {}^1/_3\, r - 0.1288\, \frac{r^2}{h_0} \tag{5}$$

accordingly, substituting for the value of h in equation (3)

$$S = \frac{rh_0dg}{2} + \frac{r^2dg}{6} - 0.1288\, \frac{r^3dg}{h_0} \tag{6}$$

This correction may be used for small capillaries, that is, those with radius less than 1 mm., but does not hold strictly for larger ones.

Richards and Coombs[12] have justified a simple treatment which involves only a correction for the measurement of the height of the meniscus itself. Letting h_0 represent the observed height and h_m equal the height of the meniscus

$$h = h_0 + {}^1/_3\, h_m \tag{7}$$

from which

$$S = rdg/2\, (h_0 + {}^1/_3\, h_m) \tag{8}$$

They have measured h_m directly and the values obtained by them show satisfactory agreement with those calculated with the Poisson formulation.

The radius of the capillaries used by us came well within the limits demanded by these formulations; accordingly, the Poisson equation was applied to our data for the calculation of capillary radius and comparisons were made between the values obtained when such meniscus corrections were applied and results obtained when no meniscus corrections were made.

Results.—Data will be given which were obtained with two different sets of apparatus (double cylinder type), designated as apparatus No. 1, and apparatus No. 2. The diameter of the capillary in No. 1 was uncorrected, 0.2530, corrected, 0.2522; in No. 2 it was uncorrected 0.3551, corrected 0.3529. In the first case there was an apparent error due to meniscus reading of -0.3%, in the second an error of -0.6%.

In the measurement of interfacial tension a meniscus is also involved, and again when water forms a zero contact angle the general shape of the meniscus is the same as that encountered in the determination of pore radius. Similar theoretical treatment was applied and similar corrections were made. It was found that in the case of liquids whose interfacial tension values ranged between 25 and 40 dynes, the corrections were well within the limits of experimental error. For example, results for the interfacial tension of benzene and water were almost identical when calculated, first, making no meniscus corrections whatsoever and, secondly, making meniscus corrections, that is, making meniscus height corrections

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[11] Poisson, "Nouvelle Theor. de l'Act. Capill.," **1831,** pp. 112.

[12] Richards and Coombs, THIS JOURNAL, **37,** 1656 (1915).

both in the calculation of radius of the capillary tube and in the subsequent calculation of the interfacial tension using this corrected radius value. It happens that in each of these cases in which the interfacial values are within the range indicated, the magnitude of the corrections for the interfacial tension values and for the capillary radius bear the same percentage relationships. In other systems having interfacial tension values outside the range indicated, the corrections for these values do not bear the same percentage relationships to the capillary radius corrections, and failure to apply the meniscus corrections in these cases does involve a perceptible error; even in these cases, however, the error is not great and the deviation still comes within the limits encountered in almost any one of the methods in present use. In fact, as shown in the table below, the deviation is not greater than errors involved in the calibration and use of different apparatus. It may be found that when liquids of an exceptional degree of purity are used and when further refinements are made and precautions are observed in the use of the apparatus, results even more consistent may be obtained.

The following table contains the results obtained with apparatus No. 1 and apparatus No. 2 (each of the double cylinder type) with six different liquids. Both corrected and uncorrected results are given.

TABLE I

INTERFACIAL TENSION VALUES OBTAINED WITH APPARATUS

Temperature, 25; apparatus No. 1; r, 0.2530 (uncorr.); r, 0.2522 (corr.)

Organic liquid against water	h (water)	h' (org. liquid)	hd-$h'd'$	S_{23} (uncorr.)	S_{23} (corr.)
Benzene	50.93	16.66	27.85	34.56	34.56
Toluene	61.47	23.84	29.04	36.04	36.04
Ether	43.05	22.13	8.50	10.55	10.62
Chloroform	29.20	18.06	25.50	31.65	31.65
Carbon disulfide	44.80	16.17	38.68	48.00	47.95
Crude petroleum oil "M"	50.04	19.73	19.70	24.45	24.47

Temperature, 25; apparatus No. 2; r, 0.3551 (uncorr.); r, 0.3529 (corr.).

Liquid	h	h'	hd-$h'd'$	S_{23} (uncorr.)	S_{23} (corr.)
Benzene	37.64	12.99	19.90	34.66	34.65
Toluene	40.10	13.78	20.74	36.12	36.10
Ether	30.10	15.33	6.09	10.61	10.74
Chloroform	23.86	17.45	18.16	31.63	31.64
Carbon disulfide	34.92	16.10	27.60	48.08	47.98
Crude petroleum oil "M"	34.61	13.25	14.06	24.50	24.54

Summary

1. A method based upon the capillary tube principle was developed for the determination of the interfacial tension of liquid-liquid systems.

2. Two somewhat different types of apparatus were designed. Both types were constructed and used in the experimental work described herein. Both gave satisfactory results.

3. The method is rapid. The apparatus can be cleaned easily. Nontransparent liquids can be used, likewise liquids of any density. The apparatus can be placed in a water thermostat and kept at constant temperature while readings are being made.

4. In constructing this apparatus, it is not essential that the diameter of the capillary be strictly uniform throughout. Calibration of capillary radius is necessary only for a given point on the capillary tube; also for work of ordinary accuracy no capillary corrections for meniscus height readings are necessary.

5. Results which have been obtained show a close agreement with what are believed to be the most accurate interfacial tension data available in the literature.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

SYNTHESIS OF HEPTANE DICARBOXYLIC ACID-1,5[1]

BY ALBERT S. CARTER

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Perkin[2] attempted to prepare heptane dicarboxylic acid-1,5 through the condensation of diethyl ethyl malonate with trimethylene bromide and subsequent condensation with diethyl malonate to yield heptane tetracarboxylic ester-1,1,5,5. This was hydrolyzed and partially decarboxylated with the formation of an acid which seemed to be ethyl pimelic acid (heptane dicarboxylic acid-1,5). This product could not be purified to yield a solid acid, such as might be expected from the melting points of the other isomers of azelaic acid, consequently Perkin expressed doubt as to the purity of his product. This work was repeated with the utmost care and it was found that the results duplicated those obtained by Perkin. It was found, however, that small amounts of nonane tetracarboxylic ester-3,3,7,7 could be isolated from the reaction product and it was thought probable that the corresponding diethyl pimelic acid might be the impurity which inhibited the crystallization of the product.

The use of trimethylene chlorobromide or the addition of the sodium derivative of ethyl malonic ester to trimethylene bromide instead of the addition of the bromide to the sodium derivative would decrease the tendency to form the nonane tetracarboxylic acid (the former was tried by Perkin), but neither of these methods would insure that none of the second-

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[1] From an investigation carried out under the direction of Professor Richard Fischer which constituted a part of a thesis presented by A. S. Carter to the Graduate School Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Perkin, *J. Chem. Soc.*, **65**, 991 (1894).