material in ethanol plus 1.0×10^{-1}, 5.0×10^{-1} and 5.0 m./l. of sodium hydroxide, respectively. In contrast to the bis-phenols existing in *cis* and *trans* forms the addition of 1.0×10^{-1} m./l. of base produces very little ionization. Also the effects of increasing the base from 1.0×10^{-1} to 5.0 m./l. are relatively much larger. However, even the heaviest concentration of base does not produce strong ionization. These observations confirm the predictions of above that such materials would be highly resistant to ionization. Since in the *cis* form the hydroxyls are bonded together and produce a cross cancellation of dipole fields the molecule as a whole possesses at most only small electric fields. It thus has the property of an essentially non-polar material.

As the hydrogen bonding behavior, as observed by infrared absorption, may be used for structure determination so also may the ionization behavior, as observed by ultraviolet absorption. The above data, for example, demonstrate how differentiation may be made between a bis phenol allowing *cis* and *trans* forms and one allowing the *cis* form only.

Acknowledgment.—Acknowledgment is gratefully made to Dr. Donald R. Stevens and Mr. A. C. Dubbs for kindly furnishing the compounds studied, to Miss E. L. Saier and Mr. A. S. Glessner, Jr., for aid in obtaining the data and to Dr. Paul D. Foote, Executive Vice-President of Gulf Research and Development Company for permission to publish this material.

Summary

A series of bis-phenol alkanes have been examined by infrared and ultraviolet absorption spectroscopy. These materials were found to exist in three distinct states, with regard to their hydrogen bonding characteristics. They exist in *cis*- and *trans*-isomeric forms and with intermolecular hydrogen bonding. This *cis*-isomeric form is one wherein the phenolic nuclei are so oriented relative to each other that there is intramolecular hydrogen bonding between the hydroxyl groups. The *trans* form is one wherein the orientation is such that the hydroxyl groups do not influence each other.

Bis-phenol alkanes with a 2,2-substitution on the bridging group or with a bridging group having a very large appendage are restricted to existence in the *cis* form only. They are shown to have been originally synthesized completely in that form.

The distribution between *cis* and *trans* forms is given for those compounds that exist in both states. The distribution in each case appears to be unique to the compound. On the basis of intramolecular hydrogen bonding whereby the two hydroxyl groups effect a cross cancellation of dipole fields it was predicted that those materials existing in the *cis* form only would be less acidic than those existing in *cis* and *trans* forms. This prediction was confirmed by ultraviolet absorption measurements on the materials in alkaline solutions.

PITTSBURGH 30, PA. RECEIVED OCTOBER 11, 1949

[CONTRIBUTION FROM KOPPERS COMPANY RESEARCH FELLOWSHIP, MELLON INSTITUTE, AND THE DEPARTMENT OF PHYSICS, UNIVERSITY OF PITTSBURGH]

The Dielectric Constant of Water at High Temperatures and in Equilibrium with its Vapor

BY G. C. AKERLOF AND H. I. OSHRY[1]

The dielectric constant of water is one of the most important parameters in all modern theories of aqueous solutions. It is known with considerable accuracy between 0° and 100°.[2,3] Data for temperatures above the boiling point are not to be found in the literature. Thus it was felt to be of considerable value to fill this gap in our knowledge of the properties of one of our most common substances.

Experimental Theory.—Ordinary methods for measuring the dielectric constant of a liquid fail when it has a conductivity as high as that of water above its normal boiling temperature. Methods involving standing waves are difficult to handle at high temperatures and pressures as in the present case. Conventional resonance methods are unsatisfactory due to variable stray capacitance errors at the high frequencies required.

Wyman[3] has described a modified resonance method utilizing a rigid reactor immersed in the liquid and where the frequency of the oscillator is matched with that of the resonant frequency of the reactor. For our purposes we adopted a variation of this method. Let us assume that we have a resonant circuit with the capacitance C, resistance R and inductance L. Its impedance z at the frequency ω is given by the expression

$$z = \left[R^2 + \left(\omega L - \frac{1}{\omega C}\right)^2\right]^{1/2}$$

The impedance will pass through a minimum when the frequency has the value

$$\omega = 1/\sqrt{LC}$$

If C_0 is the capacitance of the circuit in air and

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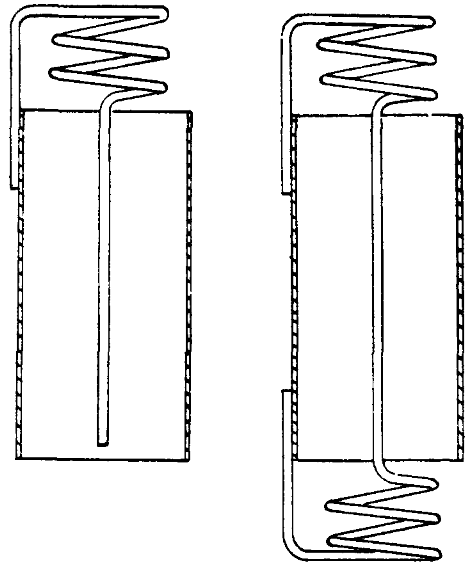
[1] From the thesis of H. I. Oshry presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Pittsburgh, Pa.

[2] Akerlof, THIS JOURNAL, **54**, 4125 (1932).

[3] Wyman, *Phys. Rev.*, **35**, 623 (1930); *cf.* Drake, Pierce and Dow, *ibid.*, **35**, 613 (1930).

C_1 is its capacitance in a medium of dielectric constant D, then C_1 is equal to C_0D. Since L is kept constant, then D equals $(\omega_0/\omega_1)^2$ where ω_0 and ω_1 are the frequencies corresponding to C_0 and C_1. The above treatment is valid only provided that the conductivity of the medium may be neglected. Wyman has shown both experimentally and theoretically that for frequencies of about one hundred megacycles per second and conductivities of the order of 10^{-4}–10^{-5} ohm cm.$^{-1}$ the error in the value of D is less than 0.2%.

Apparatus.—Two vacuum tube oscillators were used to cover the frequency range required. The low frequency oscillator employed a type 955 tube in an ultra audion circuit and covered the range from 30–300 megacycles per second. The high frequency oscillator was a modified type AN/APT5 radar jamming transmitter which has a lighthouse tube built into a pair of concentric tunable coaxial lines arranged in a tuned plate, tuned cathode circuit. This oscillator has a range of 300–750 megacycles in the fundamental and of 750–1500 megacycles in the next higher mode.



Single coil reactor Symmetrical reactor

Fig. 1.

Frequencies were measured employing a U. S. Signal Corps type I-222A heterodyne frequency meter calibrated with a built-in, five megacycle crystal oscillator. The fundamental range of the oscillator of the frequency meter covers the range 40–80 megacycles. However, various harmonics may be used to measure frequencies as high as 1500 megacycles. Approximate frequencies were first obtained with absorption-type frequency meters to determine which one of the harmonics of the heterodyne frequency meter was being used. The frequency of the crystal oscillator was compared with the five-megacycle signal broadcast by the Bureau of Standards over WWV. It was found to agree with the frequency of this signal within less than 0.01%.

The reactors, or resonators, were constructed of solid platinum sheet and wire formed and welded together as shown in Fig. 1. By varying the diameter and number of turns of the coils, resonant frequencies in air of between 400 and 1100 megacycles could be obtained. The resonators were mounted in a stainless steel pressure vessel as shown in section in Fig. 2. To couple the reactor to the oscillator or to a detector, coupling loops were attached to automotive type spark plugs which were mounted in the ends of the pressure vessel. On the outside of the latter the coupling lines, coaxial or parallel wires, were connected to the terminal of the spark plug and to the body of the pressure vessel.

The pressure vessel was mounted in the center of a cylindrical aluminum casting nine inches in diameter and sixteen inches long. The outside of the casting was covered with a double layer of asbestos paper wound with a nichrome ribbon heating element and finally insulated with magnesia pipe covering four inches thick. The power input could be varied from 0.0–4.2 kilowatts using a variable transformer.

Temperatures were measured with chromel-constantan thermocouples calibrated by comparison with a platinum resistance thermometer certified by the Bureau of Standards. Three thermocouples were used, one was mounted in the well of the pressure vessel to indicate the temperature of the water; the other two were mounted in wells in the surrounding aluminum casting to indicate the magnitude of the thermal gradients. Readings were taken under such conditions that the temperature may be considered to have been accurate within 0.2°. Pressures were measured with a 16-inch precision bourdon type gage with a range of 0–750 atmospheres. As the temperature increased during a series of measurements, small amounts of water were withdrawn from the system through sensitive needle valves in such a manner that the pressure was maintained at or close to the corresponding vapor pressure of water.

Experimental Data.—In the case of single-coil reactors resonance with the oscillator was first determined by the maximum reaction on its grid current. With this type of measurement the adjustment of the coupling between the transmission line and the reactor was found to be a highly critical factor. It was necessary to fix the coupling by trial and error so that it was tight enough to affect the oscillator appreciably without permitting mutual interactions to influ-

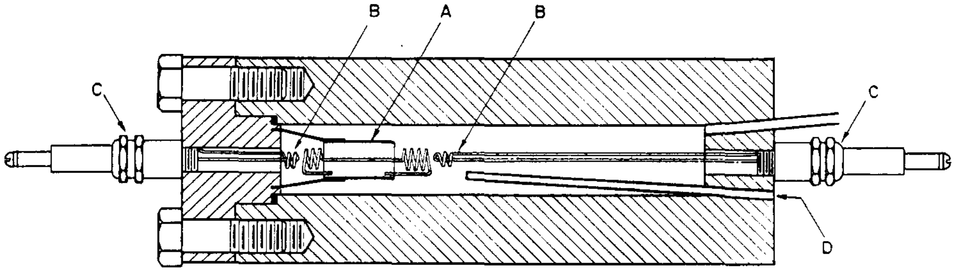


Fig. 2.—Stainless steel pressure vessel, 8″ long × 3″ o. d., 1″ i. d., showing platinum reactor, A; coupling loops, B; spark plugs, C; and thermocouple well, D.

ence the value of the resonant frequency of the reactor. In the table below is shown the effect of the degree of coupling on the resonant frequency with various coupling lines.

Line impedance in ohms	Resonant frequency of line, mc./sec.	Resonant frequency of reactor, mc./sec. Tight coupl.	Loose coupl.
450	102	85.0	71.6
300	97	80.5	71.6
72	90	77.0	71.6

As a result of this difficulty a more sensitive method was worked out for the detection of the conditions for maximum resonance. The reactor was mounted between two coupling lines, one coupled to the oscillator, the other to a sensitive mirror galvanometer through a 1N34 crystal rectifier. The sensitivity of the detector system was such that a signal of 0.5 microvolt gave a deflection of one millimeter on the galvanometer scale employed. The coupling between the oscillator and the reactor was adjusted so that the frequency of maximum rate of energy transmission was identical with the frequency of maximum reaction on the oscillator. Spurious readings were obtained when the oscillator frequency coincided with the resonant frequency of one of the transmission lines. These were discarded if they disappeared when the transmission line frequency was changed by means of a stub or by changing the length of the line.

Since our measurements were carried out over an extended range of temperatures, it was necessary to determine the variation of the resonant frequency of the reactor in air as a function of the temperature. For this purpose the reactor was mounted in the dry and empty pressure vessel and placed in the furnace. The temperature was raised slowly and the resonant frequency measured at intervals of about 50° from room temperature to about 400°. The resonant frequency of the reactor in air was found to decrease linearly with temperature over the range measured as is shown graphically in Fig. 3. When measurements were made with the pressure vessel filled with water, the corresponding values of the resonant frequency in air were taken from this curve.

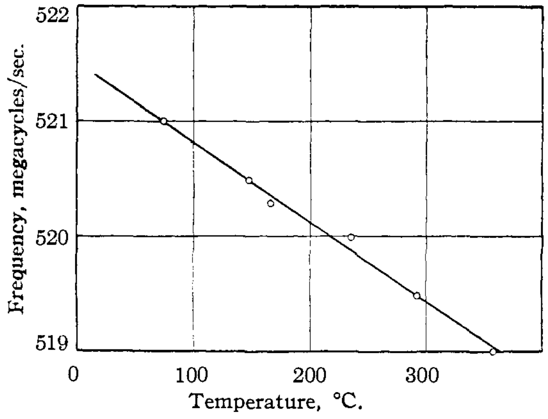


Fig. 3.—Variation with temperature of the resonant frequency of a reactor in air.

The accuracy of our experimental method was tested by mounting the reactor in the pressure vessel, filling the vessel with water re-distilled from an alkaline solution of potassium permanganate and measuring the resonant frequency at ten temperatures between 32 and 92°. The values of the dielectric constant of water at the measuring temperatures were computed from Wyman's equation and the value of the resonant frequency in air at room temperature was obtained. The average of the values found, 520.7 ± 0.2 megacycles, agrees with the measured value, 521.1 megacycles, within 0.1%. This demonstrates not only that our experimental method is valid and precise but also confirms the high accuracy of the data of Wyman.

Using several different reactors measurements of the dielectric constant of water were carried out over the temperature range from 100° up to the critical point. The resonant frequencies of the different reactors in air were about 430, 521, 650 and 840 megacycles. Between the different reactors no variation of the dielectric constant with frequency could be found. The results are shown graphically in Fig. 4. In the range between 273 and 640°K. the data obtained fit the equation

$$D = A/T + B + CT + DT^2 + ET^3$$

where the constants in order are equal to: A, 5321 (K.°); B, 233.76; C, -0.9297 (K.°),$^{-1}$, D, 0.001417 (K.°)$^{-2}$ and E, 0.0000008292 (K.°)$^{-3}$ and T is the absolute temperature in Kelvin degrees. The deviations found in the temperature range between 640–650°K. are open to question.

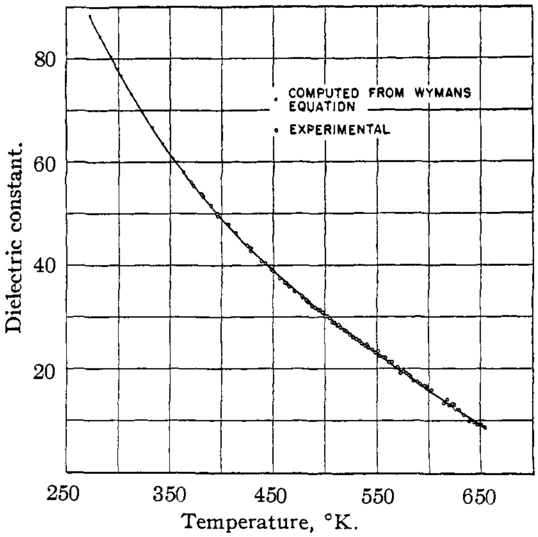


Fig. 4.—The dielectric constant of water as a function of the absolute temperature. The curve represents calculated values.

Table I

Computed Values for the Dielectric Constant of Water at Temperatures between 100 and 370°

Temp., °C.	D	Temp., °C.	D	Temp., °C.	D
100	55.39	200	34.59	300	19.66
110	52.89	210	32.93	310	18.27
120	50.48	220	31.32	320	16.88
130	48.19	230	29.75	330	15.51
140	46.00	240	28.24	340	14.10
150	43.89	250	26.75	350	12.61
160	41.87	260	25.29	360	11.22
170	39.96	270	23.86	370	9.74
180	38.10	280	22.45		
190	36.32	290	21.05		

In this range the density of the liquid and the vapor are almost identical and the deviations observed may be due to the fact that the reactor was in a mixture of the two phases. A summary of a series of computed values of the dielectric constant is given in Table I.

Acknowledgments.—We wish to express our thanks to Mr. Fred Denig, Vice President of Koppers Company, whose interest and support made the study possible, to R. C. Miller and J. W. Rex for their help in some of the experimental work.

Summary

The dielectric constant of water in equilibrium with its vapor has been determined in the temperature range from the normal boiling to the critical point. The data obtained may be expressed by the equation

$$D = 5321/T + 233.76 - 0.9297T + 0.001417T^2 - 0.0_68292T^3$$

where T represents absolute temperature $(273.1 + t)$.

PITTSBURGH, PENNA. RECEIVED SEPTEMBER 17, 1949

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Cleavage of Silicones by Hydrogen Fluoride[1]

BY HAROLD SIMMONS BOOTH AND MEYER LOUIS FREEDMAN

The functional composition is a fundamental variable in silicone production. Empirical methods for estimating this functionality are limited to pure silicones.[2,3,4] Chemical methods, such as the determination of silicon–carbon ratios, may also fail when a variety of organic substituents are present or when the silicone is compounded with other materials. Studies made of reactions which produce silicone resins by hydrolysis[5] or oxidation[6] have been handicapped by the lack of a suitable analytical method for the products. This paper describes the reaction of silicones with anhydrous hydrogen fluoride and a new method of analysis of alkyl silicones based on this reaction.

The functional composition is fully expressed by a formulation of the monomeric siloxy units which would result, hypothetically, if every oxygen atom in the silicone molecule were split in two. Hydrofluorination effects such a depolymerization. Many organofluorosilanes have been synthesized and accurately characterized.[7–12] Table I gives the relationship for the methyl silicones. On a mole basis, the composition of a methylfluorosilane mixture is the same as the formulation, in equivalent siloxy units, of the hydrofluorinated methyl silicone. The weight of methyl silicone in a compounded sample is the sum of the siloxy unit weights. These can be calculated from the yield of methylfluorosilanes obtained by the new hydrofluorination method described in this paper.

TABLE I

METHYLFLUOROSILANES AND THEIR EQUIVALENT SILOXY UNITS

Methylfluorosilane	Conversion factor	Equivalent siloxy unit	Unit symbol	Unit weight	Unit silicon, %
Me_3SiF	0.881	$Me_3SiO_{1/2}$	M	81.16	34.5
Me_2SiF_2	.772	$Me_2SiO_{2/2}$	D	74.13	37.8
$MeSiF_3$	.671	$MeSiO_{3/2}$	T	67.09	41.8

The cleavage of silicones by hydrofluoric acid in sulfuric acid solution has occasionally been used to synthesize organofluorosilanes.[13,14,15] Yields and reaction rates were low. Liquid anhydrous hydrogen fluoride, as suggested by a theoretical study, was found to convert methyl silicones rapidly and quantitatively into the equivalent methylfluorosilanes. The reaction is one of solvolysis.

$$(Si—O—Si) + 3HF \longrightarrow 2(Si—F) + H_2O\cdot HF$$

Apparatus

The bar stock reactor valve (A of Fig. 1) is connected by Saran tubing and forged brass flare type fittings, either to the 10-g. capacity hydrogen fluoride ampule (B), to a vacuum pump, or to a nitrogen supply as needed. The doorknob shaped copper reactor (C) screws into the reactor head (D), seating on a Saran gasket. The reactor head was machined from a 3-inch length of hexagonal steel bar, 1 inch in diameter. A nickel induction tube extends from the upper chamber of the reactor head into the reactor. The Saran safety manometer (E) dips 10 cm. into a reservoir of mercury (not shown) in order to obtain pressure greater than atmospheric in the reaction. The absorption tube (F) is a 3 foot length of $^1/_2$ inch i. d. nickel tubing. Moisture and hydrogen fluoride are removed from the generated gases by a 35-g. charge of Drierite

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[1] From a thesis presented by Meyer Louis Freedman to the Graduate School of Western Reserve University, September, 1949, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, and based upon work done in connection with a research project sponsored by the Office of Naval Research.

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