

that  $\beta$ -alanine is actually a cleavage product of pantothenic acid.

**Discussion.**—The fact that  $\beta$ -alanine, as a cleavage product of pantothenic acid, may show considerable biological activity in certain media and not in others, serves to explain some of the contradictions in the literature with regard to the stability of "bios" in alkaline and acid condition. It seems likely from our findings that  $\beta$ -alanine is of widespread importance in biochemistry and that its importance for various organisms is connected with the fact that it makes up a part of the pantothenic acid molecule. This question is being investigated more fully in this Laboratory.

### Summary

1. Pantothenic acid appears to be synthesized by yeast only when  $\beta$ -alanine is furnished in the culture medium.

2. Several lines of evidence indicate  $\beta$ -alanine to be a cleavage product of pantothenic acid. It finally was isolated from this source in the form of  $\beta$ -naphthalenesulfo- $\beta$ -alanine.

3. The yield of  $\beta$ -alanine from the pantothenic acid preparation of which an analysis has been reported, indicates that it was not more than 90% pure.

4. The significance of these findings for "bios" studies has been discussed briefly.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

## Electrical Properties of Multimolecular Films

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### A. Introduction

In 1935 we made some preliminary attempts to measure the dielectric constant and dielectric loss of 101 layer barium stearate films deposited on a polished chromium surface. Measurements of such films should be extremely interesting because of the known arrangement of organic molecules which normally can be measured only in conditions of random orientation. We immediately found three experimental limitations. First our existing bridge equipment had insufficient sensitivity and accuracy. Second, we needed more accurate measurement of the area of contact of a small drop of mercury used as one electrode. Third, the metal and water surfaces must be kept dust free while the film is being prepared. Occasional dust particles have little effect on optical measurements but cause conducting holes or cracks in the film which prevent electrical measurements. Nevertheless, the preliminary results were encouraging enough so that last year we refined the necessary bridge equipment,<sup>1</sup> developed a means for accurate measurement of a few square millimeters of mercury drop contact area and built a box in which films could be deposited with a much lower concentration of dust particles.

The results of recent studies on films made from a number of metal soaps, using this improved equipment, are described in this paper.

(1) S. I. Reynolds and H. H. Race, *G. E. Rev.*, **41**, 529 (1938).

**B. Preparation of Specimens.**—Multilayer films were built by depositing monolayers on a clean polished chromium slide as described by Blodgett<sup>2</sup> except that we took special precautions to prevent the deposition of dust particles in or on the film.

It was found necessary to control very closely the acidity of the water-bath from which the various types of films were made in order to obtain good reproducibility. This was done by measuring the pH of the water with a glass electrode.<sup>3</sup>

### C. Apparatus and Technique of Measurements

1. **Electrodes.**—The metal slide on which the multimolecular films were laid down constituted one electrode. A number of types of contacts were tried on the surface of the film for the other electrode. Using very thin pieces of metal foil, we were unable to get intimate contact without mechanically damaging the film, and the accurate determination of area was very difficult. Using drops of aqueous electrolytes, we were unable to find any of sufficiently low resistivity not to affect the dielectric loss measurements particularly at high frequencies. A mercury drop is the only satisfactory contact which we have found.

The electrode assembly is shown in Fig. 1. The chromium plated slide on which the film is built is held in a microscope stage, which is insulated from the base plate by mica strips. The mercury drop upper electrode is suspended from an amalgamated copper rod which can be lowered by a micrometer screw to make contact with the film surface. The upper electrode assembly is insulated from the base plate by long Pyrex rods. The whole assembly is mounted on a heavy cast iron base to prevent vibration and changes in area of the mercury drop contact during measurements.

(2) K. B. Blodgett, *THIS JOURNAL*, **57**, 1007 (1935).

(3) D. A. MacInnes and M. Dole, *ibid.*, **52**, 29 (1930).

**2. Measurement of Mercury Drop Contact Area.**—In order to work within the capacitance limits of the bridge equipment, the mercury drop contact area had to be small since the capacitance per unit area of these thin films is

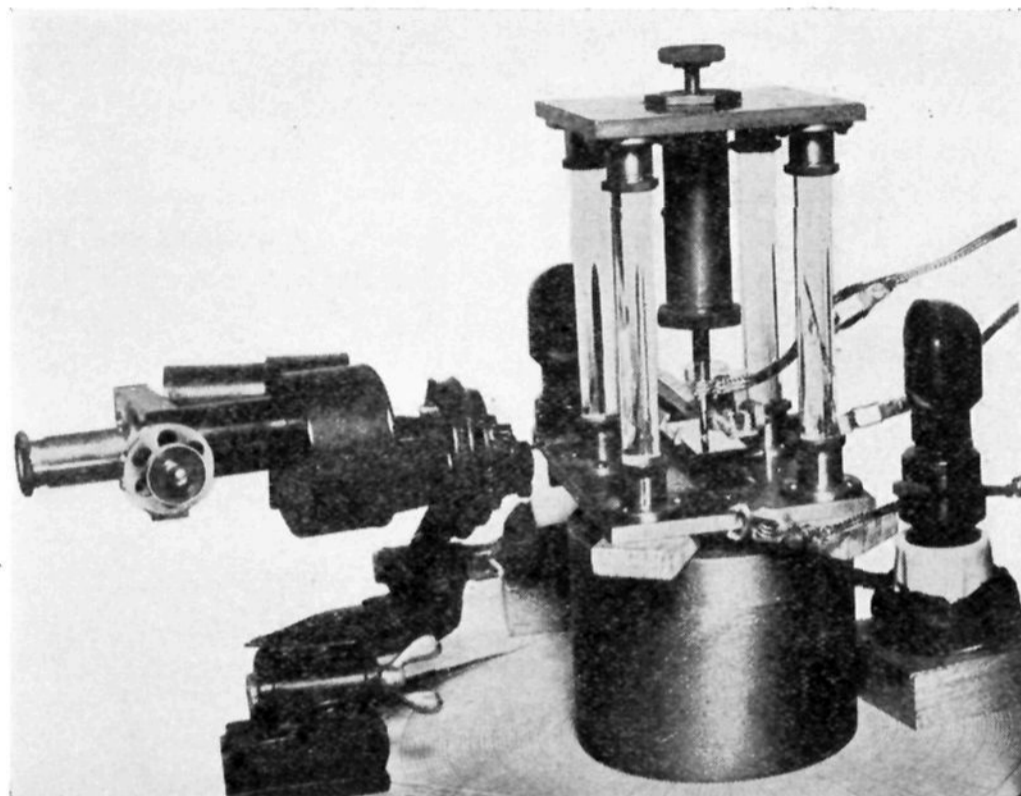


Fig. 1.

very high. Also, in order to calculate the dielectric constant from such capacitance measurements the contact area and the thickness of the film must be measured very accurately. It was found by experience that the contact area might not be circular. Therefore a filar microscope with a horizontal micrometer feed was set up on a separate support so that the drop could be viewed from two 90° positions at an angle slightly above the plane of the film surface. In each position the drop is illuminated from the rear to give a sharp silhouette in the field of the microscope. These diameters were averaged to calculate the area of contact of the drop.

**3. Measurement of Film Thickness.**—The thickness per layer of various metal soap films has been accurately determined by index of refraction measurements.<sup>4</sup> Two acids of different carbon chain length were used to form the films reported in this paper. The thickness per layer for stearic acid is  $24.2 \times 10^{-8}$  cm., and for arachidic acid is  $26.9 \times 10^{-8}$  cm.

The total thickness of a given film is obtained by multiplying these values by the number of layers applied. To check these thicknesses, interference color step gages have been prepared for direct optical comparison with the films to be measured.

**4. Electrical Bridge Measurements.**—Capacitance and resistance measurements were made over a frequency range from 40 to 1,000,000 cycles per second by means of special guarded bridges.<sup>1</sup> From these measurements the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) of the films were calculated from the equivalent parallel circuit.<sup>5</sup>

(4) K. B. Blodgett, "Built-up Films of Barium Stearate."

(5) H. H. Race and S. C. Leonard, *Elec. Eng.*, **55**, 1347 (1936).

The low potential test lead is connected to the chromium plate, and the guard lead is connected to the base plate of the film holder (see Fig. 1) with the high potential lead connected to the mercury electrode holder.

By balancing the guard and test circuits of the bridges the chromium plate and base plate of film holder are brought to the same potential, thus eliminating from the measurements any possible losses in the mica insulation between the movable stage and base plate. At the same time the losses caused by the glass supports from the high potential electrode are shunted to the guarded base plate and thus do not affect the loss measurements of the film. Zero measurements are made with the mercury drop just above the film.

**5. Dielectric Strength Tests.**—D. c. breakdown tests are also made using the electrodes shown in Fig. 1. Voltage may be varied from 0.01 v. up and is obtained from a fine potentiometer and measured on a high resistance voltmeter.

For a. c. breakdown measurements the voltage is supplied by a beat frequency oscillator. The output voltage is controlled by a potentiometer

on the oscillator panel and is measured with a vacuum tube voltmeter.<sup>6</sup>

#### D. Experimental Results

**1. Reproducibility of Dielectric Constant Measurements.**—To obtain a clean drop of mercury as an upper electrode the amalgamated copper rod was washed with clean mercury before each measurement. Also the surface of the slide was blown dust free by a small jet of filtered air. If dust particles, visible under the microscope, are left between the drop and the film, reproducible electrical measurements are impossible. With extreme care typical variations between successive dielectric constant ( $\epsilon'$ ) measurements at different points of the same film are shown in Figs. 2 and 3. The standard deviations are 2% or less, which represents the over-all accuracy of the area, thickness and electrical measurements. Variations of dielectric constant measurements with area of the mercury drop on the same film are shown in Fig. 4 and indicate no systematic error.

Each of the above comparisons was made by taking measurements on different areas on the same film. Wider variations of electrical properties are often found on different films of the same

(6) General Radio Type 726A.

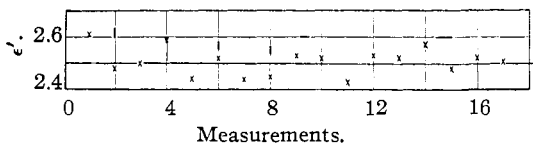


Fig. 2.—Variation in successive  $\epsilon'$  measurements on a calcium stearate film: 67 X-layers, pH 9.0 (buffered), bath  $10^{-4} M$   $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , av.  $\epsilon' = 2.50$ ,  $\sigma = 2.2\%$ .

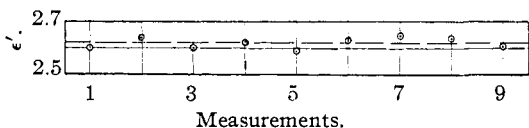


Fig. 3.—Variation in successive  $\epsilon'$  measurements on a lead stearate film: 101 Y-layers, pH 5.02 (buffered), bath ( $10^{-4} M$   $\text{PbCl}_2$ ,  $10^{-4} M$   $\text{FeCl}_2$ ,  $2 \times 10^{-5} M$   $\text{HCl}$ ,  $5 \times 10^{-3} M$   $\text{KI}$ ), av.  $\epsilon' = 2.62$ ,  $\sigma = 0.8\%$ .

material made at different times, as shown by Fig. 5. The standard deviation among these is 4.3%. It will be observed on subsequent graphs

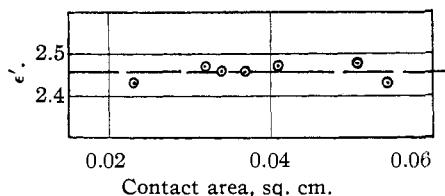


Fig. 4.—Variation in  $\epsilon'$  measurements with area of mercury drop on a cadmium arachidate film: av.  $\epsilon' = 2.46$ ,  $\sigma = 0.08\%$ .

that, in general, there is better agreement between measurements taken at different spots of the same film than is found between different films. It was found that control of the acidity of the bath was very important not only in the building of multi-layer films but also in the electrical properties of such films. For the more recent tests the pH of the bath is recorded on the data sheets. In Fig. 6 are shown dielectric constant data for (X) and

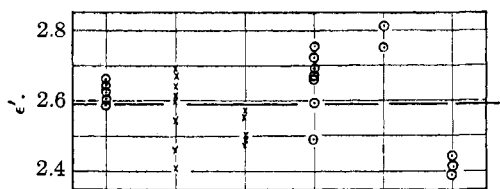


Fig. 5.—Variation in  $\epsilon'$  measurements on different films of cadmium stearate: bath  $10^{-4} M$   $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (not buffered), av.  $\epsilon' = 2.59$ ,  $\sigma = 4.3\%$ .

(Y) layers of barium stearate. We think that the difference between these two sets of data does not result from differences in the direction of orientation but rather that it is a function of the pH of the bath from which the films were made since we know that the proportion of soap to acid in the films varies considerably with changes in hydrogen ion concentration<sup>7</sup> of the bath.

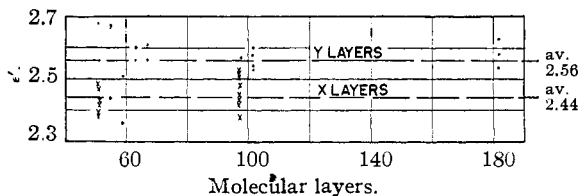


Fig. 6.—Variation in  $\epsilon'$  measurements on different thicknesses of (X) and (Y) barium stearate films (buffered): ● for Y-films—pH 6.9, bath  $10^{-4} M$   $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $2 \times 10^{-4} M$   $\text{KHCO}_3$ ; × for X-films—pH 9.0, bath  $10^{-4} M$   $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $3 \times 10^{-3} M$   $\text{KHCO}_3$  and 2 drops per liter of concd.  $\text{NH}_4\text{OH}$ .

During the latter part of this work the films were taken off from buffered solutions so that no changes should occur in the constitution of successive layers. Such changes may account for some of the variations observed when films were built up from unbuffered solutions.

**2. Dielectric Constant Independent of Thickness.**—Figures 5 and 6 show that within the reproducibility and accuracy of our measurements the dielectric constant is independent of the film thickness between 51 and 181 layers. We have additional data corroborating this statement for films varying from 21 to 201 layers. This indicates also that, when properly dust free, there is no air between the film and the mercury drop.

**3. Dielectric Constant Independent of Frequency.**—The dielectric constant of a number of films was measured within the frequency range from 40 to  $10^6$  cycles per second. The data are plotted in Figs. 7, 8 and 9. Again, within the reproducibility and accuracy of our measurements, the dielectric constant is independent of frequency up to  $10^6$  cycles per second.

**4. Dielectric Loss Independent of Thickness and Frequency.**—Each measurement of dielectric constant reported above was accompanied by a dielectric loss measurement made simultaneously. These represent independent properties of the films and are plotted against frequency in Figs. 10, 11 and 12. The losses show larger deviations

(7) I. Langmuir and V. J. Schaefer, *THIS JOURNAL*, **58**, 284 (1936).

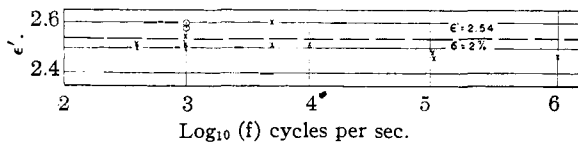


Fig. 7.—Variation in  $\epsilon'$  with frequency on copper stearate films (not buffered): bath  $10^{-4} M$   $CuCl_2 \cdot 2H_2O$ ,  $\odot$  for 61 Y-layers with  $pH$  5.38,  $\times$  for 101 Y-layers with  $pH$  4.68.

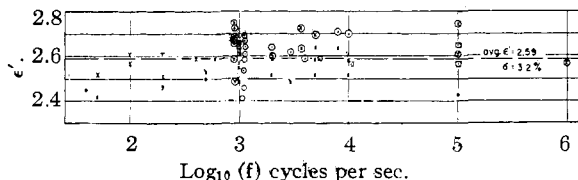


Fig. 8.—Variation in  $\epsilon'$  with frequency on cadmium stearate films (not buffered): bath  $10^{-4} M$   $CdCl_2 \cdot 2H_2O$ ,  $\square$  101 layers on 3-3-38,  $\odot$  61 layers on 4-25-38,  $\times$  61 layers on 5-2-38,  $\oplus$  101 layers on 6-27-38.

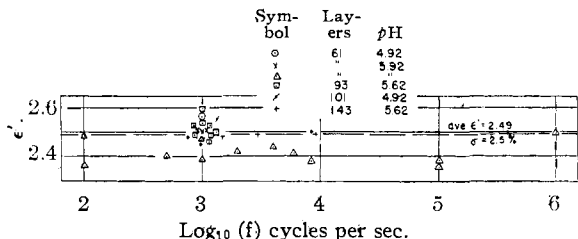


Fig. 9.—Variation in  $\epsilon'$  with frequency on cadmium arachidate films (not buffered).

between measurements on the same film or on different films than was found for the dielectric constant. However, these deviations appear to be random and show no dependence upon either thickness or frequency. The order of magnitude of  $\tan \delta$  is low, being usually less than 0.001. The accuracy and sensitivity of the bridges used are considerably better than this value,<sup>1</sup> so that we believe the films are electrically non-uniform to this extent.

The dielectric loss measurements on dry multi-layer films are of a much smaller order of magnitude than those obtained by Haskins<sup>3</sup> and his co-workers. Assuming that they reported equivalent parallel resistance and capacitance of the films, their data indicate a two-fold variation in dielectric constant and a 15-fold variation in  $\tan \delta$  as functions of the number of layers, and the order of magnitude of  $\tan \delta$  is from 1000 to 10,000 times higher than the values reported in this paper. We believe that the wide differences in

(8) Buckwald, Gallagher, Haskins, Thatcher and Zahl, *Proc. Nat. Acad. Sci.*, **24**, 204 (1938).

the two sets of data are caused by the electrolyte in which their films were immersed.

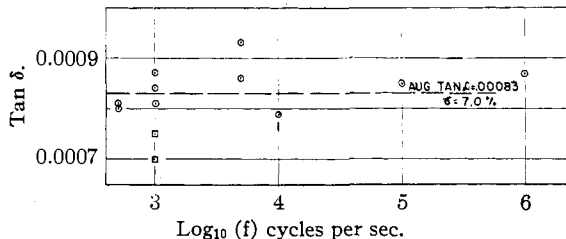


Fig. 10.—Variation of  $\tan \delta$  with frequency on copper stearate films: bath  $10^{-4} M$   $CuCl_2 \cdot 2H_2O$ ,  $\odot$  101 Y-layers at  $pH$  4.68,  $\square$  61 Y-layers at  $pH$  5.38.

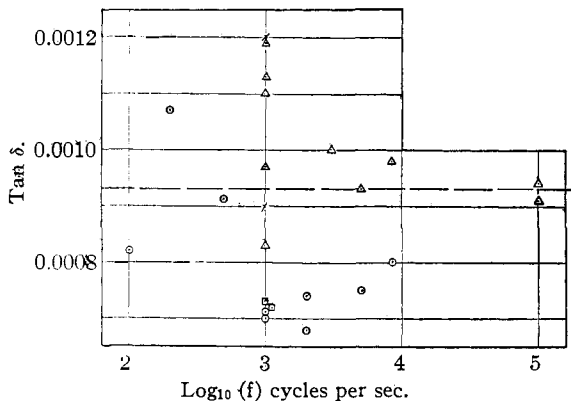


Fig. 11.—Variation in  $\tan \delta$  with frequency on cadmium stearate films: av.  $\tan \delta = 0.00093$  and  $\sigma = 17\%$ , bath  $10^{-4} M$   $CaCl_2 \cdot 2H_2O$ .

Symbol	Layers	pH
$\odot$	61	6.12
$\triangle$	101	?
$\square$	101	?
$\times$	59	5.20

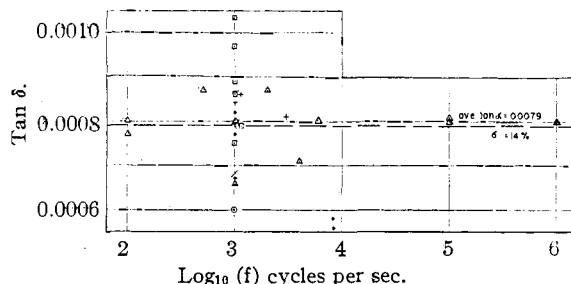


Fig. 12.—Variation in  $\tan \delta$  with frequency on cadmium arachidate films: bath  $10^{-4} M$   $CdCl_2 \cdot 2H_2O$  (not buffered).

Symbol	Layers	pH
$\odot$	61	4.92
$\times$	61	5.92
$\triangle$	61	5.92
$\square$	93	5.62
$\times$	101	4.92
$\oplus$	143	5.62

5. **Attempt to Use Glass Slide with Evaporated Chromium Surface.**—In an attempt to get a highly polished metal surface on which to form the films we tried microscope slides on which a coating of chromium had been obtained by vaporization. It was found that metal films thin enough to adhere to the glass without peeling or cracking had an electrical resistivity which was too high to permit high frequency dielectric loss measurements, as indicated in Fig. 13.

6. **Effects of Skeletonization.**—Langmuir and Schaefer<sup>7</sup> have shown the dependence on the hydrogen-ion concentration of the bath of the conversion of fatty acids to metallic soaps. For example, if a film of cadmium arachidate which has been built at pH 5.62 is soaked for one to ten seconds in a solvent such as benzene and is then taken from the benzene, the color of the soaked film is much different from that of the original film. The change is due, according to Blodgett and Langmuir,<sup>9</sup> to a large decrease in the refractive index of the film, the actual thickness being unaltered. The benzene dissolves the arachidic acid, leaving cadmium arachidate as a skeleton with air filling the spaces previously occupied by the arachidic acid.

For this concept of the structure of a skeletonized film the remaining soap can be considered to be paralleled by the air spaces, and the dielectric constant of such a film is given by the relation

$$\epsilon'_1 = \epsilon'_0(d_1/d_0) + \epsilon'_a(1 - d_1/d_0) \quad (1)$$

where  $\epsilon'_0$  = dielectric constant of unskeltonized film,  $\epsilon'_1$  = dielectric constant of skeletonized film,  $\epsilon'_a = 1$  = dielectric constant of air, and  $(d_1/d_0)$  = ratio of densities of skeletonized to unskeltonized films. Therefore calculations of  $\epsilon'$  can be made on the above assumptions for comparison with actual measurements on films after skeletonization. In order to do so it is necessary to convert the observations of changes in apparent thickness caused by skeletonization to changes in density in order to determine the proportion of the volume of the skeleton occupied by air. Such calculations have been made by Blodgett<sup>10</sup> and the results are given in Table I.

The proof that a skeletonized film did not collapse lay in the fact that the original optical thickness was restored by allowing a drop of oil to run over the film and thus refill the spaces originally

(9) K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 980 (1937).

(10) K. B. Blodgett, "Use of Interference to Extinguish Reflection of Light from Glass" (not yet published.)

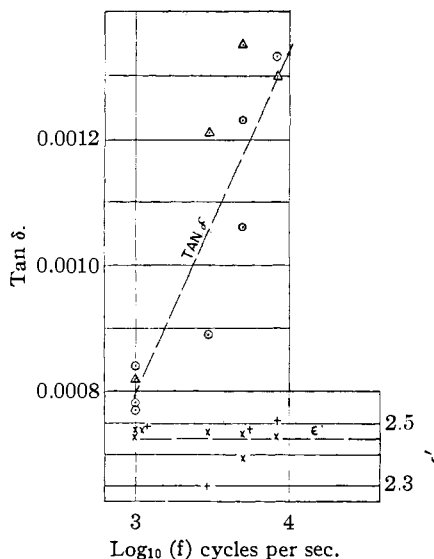


Fig. 13.—Effect of using vaporized chromium surface on glass slide for film base: bath  $10^{-4}$  M  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ .

Ordinate	Symbol	Layers	pH
$\tan \delta$	$\Delta$	45	5.75
$\tan \delta$	$\circ$	81	5.63
$\epsilon'$	$\times$	45	5.75
$\epsilon'$	$+$	81	5.63

occupied by acid molecules. After this refilling the dielectric constant can again be measured and a check calculation made by substituting for  $\epsilon'_a$  in Equation 1 the dielectric constant of the oil.

TABLE I  
RELATIVE DENSITY OF SKELETONIZED FILMS FROM APPARENT THICKNESS (ANGLE OF INCIDENCE =  $80^\circ$ ;  $n_0 = 1.50$ )

$\frac{\eta_1 - 1}{\eta_0 - 1}$	Ratio of apparent thickness after and before skeletonization ( $t_1/t_0$ )	Ratio of densities after and before skeletonization ( $d_1/d_0$ )
1.0	1.0	1.0
0.9	0.9404	0.9136
.8	.8793	.8242
.7	.8159	.7317
.6	.7500	.6358
.5	.6804	.5369
.4	.6058	.4349

Table II shows the data obtained on several films of cadmium arachidate made at pH 5.7, with check calculations made as indicated above. Columns (1) and (2) give the apparent thickness in number of layers before and after skeletonization obtained by visual comparison with step gages. Column (4) gives the ratio of densities as determined from a plot of the data in Table I.

Columns (5) and (6) give the measured dielectric constants before and after skeletonization, calculated on the basis that the actual thickness

TABLE II  
ELECTRICAL DATA ON UNSKELETONIZED (0) AND SKELETONIZED (1) FILMS OF CADMIUM ARACHIDATE

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8) Filled with non-polar oil	(9)	(10) Filled with tetrachloro- diphenyl	(11)
	Optical thickness $t_0$	$t_1$	$(t_1/t_0)$	$(d_1/d_0)$	$\epsilon'_0$ Measd.	$\epsilon'_1$ Measd.	$\epsilon'_1$ Calcd.	$\epsilon'_2$ Measd.	$\epsilon'_2$ Calcd.	$\epsilon'_2$ Measd.	$\epsilon'_2$ Calcd.
A	75	53	0.707	0.574	2.48 2.48 2.47 2.49	1.69 1.74 1.71 1.87 1.73	1.85	2.29 2.20 2.19	2.34		
B	61	43	.705	.571	2.44 2.43 2.47	1.62 1.68 1.69	1.82	2.25	2.31	3.04 3.25	3.63
C	61	51	.837	.764	2.50 2.50 2.50	1.96 1.94 2.02 1.97	2.15	2.32 2.38	2.42		
D	59	51	.86	.797	2.49	2.10	2.18				

does not change. Column (7) gives the dielectric constant of the skeletonized film calculated from Equation 1. The agreement between measured and calculated values appears to be sufficiently close to constitute a check on the concept of the structure of a skeletonized film and the assumption that the remaining soap and air are electrically

considerably higher than the measured value, indicating a reduction of polar orientation of the liquid within the matrix of cadmium arachidate molecules.

#### 7. Dielectric Strength Measurements.—

Throughout this work we have found that even after taking considerable care to prevent the inclusion of dust in the multilayer films, dielectric strength measurements were very non-uniform. It also appears that the proportion of conversion to soap, determined by the  $pH$  of the bath, has an effect on the dielectric strength. The results of a number of measurements on films of cadmium arachidate made from baths whose  $pH$  varied from 5.1 to 6.62 are plotted in Fig. 14. While some low values were obtained on films made at all  $pH$ s, the highest dielectric strengths were obtained only at the higher  $pH$ s, which correspond to higher proportions of converted soap.

The expected lowering of dielectric strength by skeletonization is illustrated in Fig. 15. The circled numbers indicate the position on the slide and the sequence of measurement.

To determine whether the dielectric strength is a function of frequency, the measurements shown in Fig. 16 were made. It appears that the d. c. values were higher on the average. However, the highest individual measurement was obtained at 1000 cycles and the large variations and limited data prevent drawing any conclusions as to the effect of frequency.

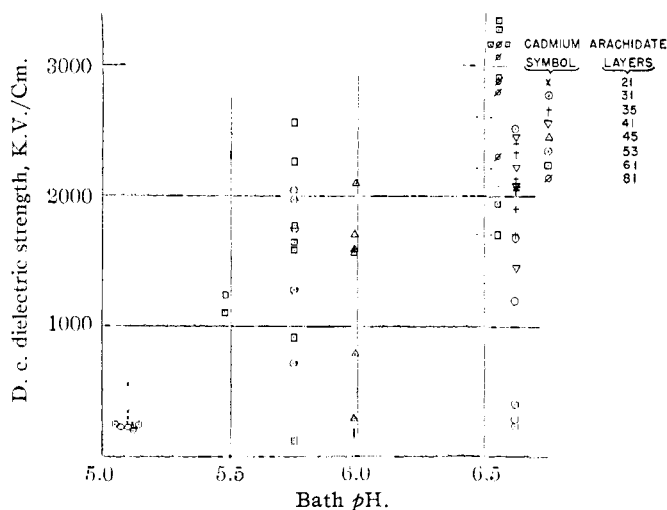


Fig. 14.—Variation in dielectric strength of cadmium arachidate films with  $pH$  of the bath.

in parallel. If the air spaces in the skeletonized film are refilled with a non-polar oil having a dielectric constant of 2.15, the dielectric constant of the film is increased as indicated in columns (8) and (9). In the case of film B a portion of the skeletonized area was refilled with a polar liquid (tetrachlorodiphenyl) having a dielectric constant of 5.22. In this case the calculated value was

TABLE III  
SUMMARY OF DIELECTRIC CONSTANT AND DIELECTRIC LOSS DATA

Material	No. of meas.	Films		Bath		Dielec. const.		Dielec. loss		Fig. no.
		No.	Type	pH	Buff-ered	Av. $\epsilon'$	$\sigma$ , %	Av. $\tan \delta$	$\sigma$ , %	
Calcium stearate	17	1	X	9.0	Yes	2.50	2.2	....	..	2
Lead stearate	9	1	Y	5.02	Yes	2.62	0.8	....	..	3
Barium stearate	17	1	Y	6.9	Yes	2.56		....	..	6
Barium stearate	14	1	X	9.0	Yes	2.44		....	..	6
Copper stearate	12	2	Y	..	No	2.54	2	0.0008	7	7 & 10
Cadmium stearate	63	4	X	..	No	2.59	3.2	.0009	17	8 & 11
Cadmium arachidate	30	6	X	..	No	2.49	2.5	.0008	14	9 & 12

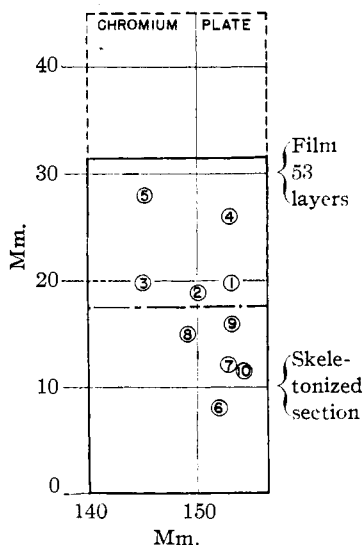


Fig. 15.—Decrease in dielectric strength of cadmium arachidate film with skeletonization at pH 5.75.

Position	P.c. Normal film treatment	K.V./cm.	Position	P.c. Skeletonized	K.V./cm.
1		1270	6		680
2		1970	7		183
3		1760	8		1060
4		2040	9		510
5		710	10		850
Av. K.V./cm.		1550	Av. K.V./cm.		654

In general the dielectric strength measurements were disappointing. The highest gradients obtained were no greater than have been found for sheet materials such as mica of considerably greater thickness. Nevertheless, 201-layer multimolecular films have been built which would withstand from 150 to 190 volts in spots. Using such films as practical capacitor dielectrics seems remote because of the difficulty of making large areas absolutely free from holes, cracks or dust particles.

E. Summary

1. Electrical measurements on multilayer molecular films are made possible by the use of a

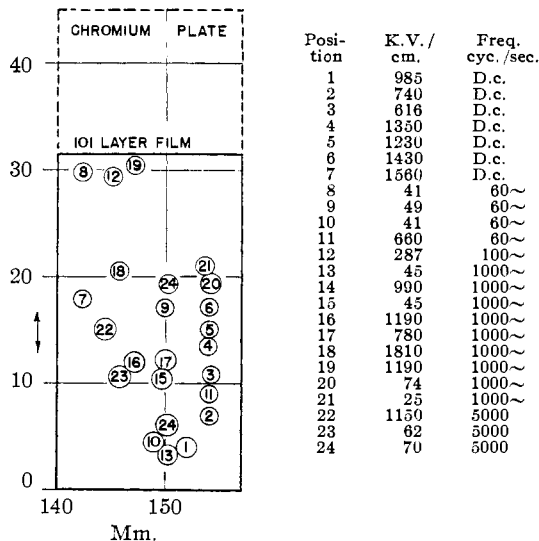


Fig. 16.—Dielectric strength of copper stearate film at several frequencies and pH 5.78.

clean mercury drop electrode. Special precautions for eliminating dust from the films during building and testing were found necessary.

2. The dielectric constant of multilayers, built up from monomolecular films of stearic and arachidic acids spread on substrates containing barium, cadmium, calcium, copper and lead, is 2.55 with standard deviations ( $\sigma$ ) = 3% (see Table III). Variations apparently depend more upon the pH of the substrate, and therefore the proportion of acid to soap in the film, than upon the metal.

3. The dielectric constant is independent of thickness and of frequency up to  $10^6$  cycles per second.

4. The dielectric losses are of the order of  $\tan \delta = 0.0009$  with standard deviations  $\sigma = 17\%$ . Within the reproducibility of the measurements there is no apparent dependence of dielectric loss upon frequency or film constitution.

5. Dielectric strengths as high as  $2 \times 10^6$  volts/cm. can be obtained. The extreme varia-

tions in dielectric strength probably are caused by holes, cracks, or dust particles in the films. In general, films with the highest dielectric strength were made from baths of higher pH.

6. Skeletonized films have electrical properties in agreement with the concept of their physical structure.

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## The Thermodynamic Constants of Bromine Chloride. The Equilibrium Reaction between Nitric Oxide, Bromine, Chlorine, Nitrosyl Bromide and Chloride, and Bromine Chloride

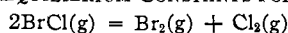
BY CARROL M. BEESON AND DON M. YOST

### Introduction

The degree of dissociation of gaseous bromine chloride, BrCl, at room temperature has been determined by several investigators by light absorption methods, and the results are in fair agreement. The use of chemical methods for studying the equilibrium has so far been restricted to studies at rather high temperatures, namely, 500 and 800°. In these determinations mixtures of fused chlorides and bromides, for example the silver chloride-silver bromide pair, are in equilibrium with

The results of all former measurements of the equilibrium constant of reaction (1) are summarized in Table I. The weighted mean value of  $K$  at room temperature was obtained by giving to each value a weight inversely proportional to the stated error; the two widely different values of Jost were omitted in calculating the mean. This method of estimating the mean is not free from criticism, but it appears to be as satisfactory as any in arriving at a value that is representative of those obtained by all investigators.

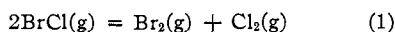
TABLE I  
SUMMARY OF EQUILIBRIUM CONSTANTS FOR THE REACTION



$$K_{\text{BrCl}} = P_{\text{Br}_2}P_{\text{Cl}_2}/P_{\text{BrCl}}^2$$

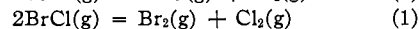
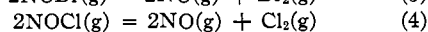
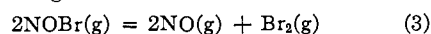
Date	Authors	Method	Temp., °C.	K
1930	Gray and Style <sup>1</sup>	Light absorption	Room	0.132 to 0.125
1931	Jost <sup>2</sup>	Light absorption	Room	.10 to .22
1933	Dickinson and Murdock <sup>3</sup>	Light absorption	Room	.12 ± 0.01
1934	Vesper and Rollefson <sup>4</sup>	Light absorption	28	.107 ± .002
1935	Braner and Victor <sup>5</sup>	Light absorption	Room	.144 ± .003
1935	Jellinek and Schütza <sup>6</sup>	KCl(l), KBr(l), Br <sub>2</sub> (g), Cl <sub>2</sub> (g), BrCl(g), and other salt pairs	800	.12
1938	Schütza <sup>7</sup>	AgCl(l), AgBr(l), Br <sub>2</sub> (g), Cl <sub>2</sub> (g), BrCl(g), also PbCl <sub>2</sub> , PbBr <sub>2</sub> , and other salt pairs	500	.1325
			800	.140
		Weighted mean value at room temperature		.126

gaseous chlorine, bromine, and bromine chloride. A knowledge of the activities of the component salts is necessary in order to evaluate the partial pressures of the three gases. The reversible gas reaction under consideration is



$$K_{\text{BrCl}} = \frac{P_{\text{Br}_2}P_{\text{Cl}_2}}{P_{\text{BrCl}}^2} \quad (2)$$

In the present paper are described the results of equilibrium measurements on the gaseous system nitric oxide, bromine, chlorine, nitrosyl bromide and chloride, and bromine chloride in the temperature range from 372 to 492°K. The reversible reactions taking place may be regarded as the following



and measurements of the total pressure of the system together with a knowledge of its composition make possible the calculation of  $K_{\text{BrCl}}$ .

(1) Gray and Style, *Proc. Roy. Soc. (London)*, **A123**, 582 (1929).

(2) Jost, *Z. physik. Chem.*, **A153**, 143 (1931).

(3) Dickinson and Murdock, private communication.

(4) Vesper and Rollefson, *THIS JOURNAL*, **56**, 620 (1934).

(5) Brauer and Victor, *Z. Elektrochem.*, **41**, 508 (1935).

(6) Jellinek and Schütza, *Z. anorg. Chem.*, **227**, 52 (1936).

(7) Schütza, *ibid.*, **239**, 245 (1938).