

THE EFFECT OF ADSORPTION ON THE ELECTRICAL
CAPACITANCE OF LIQUID SURFACES

by

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INTRODUCTION

It has been known for some time that many molecules possess permanent electric moments due to the separation of the positive and negative charges within the molecule, or the attachment at some point on the molecule, of a radical carrying a charge.

In surface active materials, in many cases, these molecules orient themselves in such a way that the charges are perpendicular, or nearly so, to the surface with all like charges oriented in the same manner.

This effect should be capable of measurement. It has been measured many times as a potential difference across the interface of the liquid in question. However, it seems that this orienting effect of the molecules possessing such electric moments should also be capable of measurement due to the effect they should have upon a condenser at the interface.

The literature available on the subject seems to show that no such measurements have been made. All the work has dealt with the potential difference across the interface rather than capacitance effects at such an interface.

It is the purpose of this thesis to attempt to devise a method capable of making such measurements due to the capacitance effects at oriented liquid surfaces, present some of the possibilities of the apparatus and a limited amount of data on such effects at the surfaces of liquid solutions.

THEORY

Faraday first discovered that the attraction or repulsion between two electric charges varies with the nature of the intervening material called the dielectric. If q_1 and q_2 represent two charges which are separated by a distance d , the force of attraction or repulsion, f , is given by the equation $f = \frac{1}{D} \cdot \frac{q_1 q_2}{d^2}$, where D is a specific property of the medium called the dielectric constant. The dielectric constant of air has been taken as unity.

Debye (1929) in summarizing the work on polar molecules attributes the dielectric constant to two factors. First, it depends on the induced polarity, which is the polarization or separation of the negative and positive charges within the molecules when an electrical field is applied to the material, and second, to a permanent polarization or separation of the positive and negative elec-

tricity due to the molecular structure.

This permanent separation of charges gives the molecule a permanent electric moment which is a measurable quantity. The moment due to the application of an electric field may be determined also but any change in temperature or any force which will cause an agitation of the molecules will change the electric moment due to such effects. Thus, any permanent electrical polarity may be calculated by a calculation of the dielectric constant of the material at several different temperatures and thus account for the amount of the dielectric constant that is dependent upon the permanent set of the charges and the amount dependent upon the separation due to the electrical field. The electric moment of many molecules has been measured and many data are available regarding the moments of different materials.

It has been known for some time that the capacity of a condenser is affected by the nature of the medium between the plates. The formula for the capacity of a condenser contains a term, K , which is, in reality, a measure of such effects. This formula is given as $C = \frac{KA}{4\pi d}$, in which A is the area of the plates and d is the distance between them.

If a material which exhibits polar properties is

placed between the plates of a condenser and one plate is charged positively, with the other negative, the molecules orient themselves so that the positive charges are pointed toward the plate that has the negative charge. Some of the negative charges on the plate will be neutralized by induction and the condenser can be then made to take a still larger charge on the plates. The capacity of the condenser has been increased because of the polar effect of the molecules. If we then measure the capacity of the condenser and compare the capacity with the reading taken in air we may calculate the dielectric constant. From the measure of the dielectric constant the dipole moment may be calculated by the Debye (1929) equation.

The largely accepted means of measuring such a change in capacity has been to measure the capacity of the condenser in air and in the material under investigation. The dielectric constant is then found by the ratio C_x/C , where C_x is the capacity in the material and C is the capacity in air.

The measurement of capacity may be accomplished in two ways. First, by the usual capacity bridge, a method for measuring capacity in very much the same manner that we measure resistance with the Wheatstone bridge, second, by

tuning a circuit to resonance, and third, by the heterodyne beat method.

The heterodyne beat method has been developed to a high degree of perfection by Williams and Weissberger (1928), Williams (1930) and Smyth (1931) and is quite satisfactory for dielectric constants that do not approach too high a value. The method has the advantage of being easy to handle, reliable and quite rapid. Because of these facts, as well as the adaptability of this type of apparatus for the present investigation, it has been chosen, with a few modifications, as the method of measuring the changes in capacity.

The theory back of the heterodyne beat method may be explained by the following. The frequency of an electron tube oscillator is determined by certain circuit values. These include the capacity of the condenser, the inductance and resistance of the circuit. If the resistance and inductance are fixed, any change in frequency must come from a change in capacitance. Thus, if we have two oscillators, one oscillating at a frequency of 1,000,000 cycles and another at 1,001,000, a beat note of 1,000 cycles will be heard. This frequency is in the audible range and may be heard in a pair of headphones. If we increase the capacity

of the oscillator operating at a frequency of 1,001,000 cycles the beat note will be lowered and as the capacity is increased even more the beat note will become lower and lower until no beat will be heard in the phones. Further increasing of capacity will again cause a beat note to appear, and the pitch will gradually rise. The point at which no sound is audible, between the two beats on either side, will be the point at which the two oscillators will be tuned to the same frequency. By proper adjustments this position of zero beat may be made to occur at a point. The condensers may thus be adjusted at the point which gives silence and the capacity measured, then the material under investigation may be placed between the plates and again the oscillator may be tuned to silence and this capacity determined. With these readings the dielectric constant may then be calculated.

Many polar molecules have also been shown to exhibit orientation at liquid surfaces both in adsorbed films as well as monomolecular films of insoluble compounds.

A great deal of our knowledge of such phenomena must be credited to Harkins, Rideal, Schulman, Langmuir and Adam as well as others. This work, up to 1930, has been placed in convenient form for study by Adam (1930).

These works point to the same conclusion in the cases of many compounds: That films are oriented, in such materials, in the surface of liquids so that one charge is above the surface with the other charge oriented into the liquid. If such is the case, then a condenser at the interface, with one plate immediately above the surface, and with the liquid acting as the lower plate, should exhibit a change in capacity due to the effects the charges in the surface layer have on the condenser at the interface.

Since we already know the dipole moments of many of these materials it seems that there should be some relation existing between them and the capacity of such an interfacial condenser. If there is any measurable change in capacity, the change could be measured by the heterodyne beat method and results tabulated in an attempt to determine if such a method can be successfully used to investigate phenomena at liquid surfaces.

Although the effect on the capacity would doubtless be very small, it appears that the measurement of such effects could be made, if proper precautions are used to have correct circuit values in the oscillators and the usual precautions taken in handling the surface films.

Providing then, that careful work and proper precau-

tions are taken in the handling of the materials and apparatus, it appears, theoretically at least, that there should be changes in capacity of an interfacial condenser because of monomolecular films of some materials containing dipole moments, and that such capacitance effects could be useful in a study of surface phenomena.

APPARATUS

The apparatus designed consisted of two oscillators (figures 1 and 2) and an experimental condenser so arranged that a liquid could be used as one plate of the condenser.

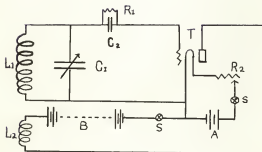
The one oscillator (figure 1), which we shall call the transmitting oscillator in this paper, was designed in order to provide a definite fixed frequency of oscillation and, at the same time, be variable enough to allow its use for later experiments in measuring dielectric constants.

The second oscillator, which we shall call the receiving oscillator, is connected to the experimental condenser and also has a pair of headphones in the plate circuit in order to provide a means of tuning the two oscil-

lators to resonance. It will be noticed that outside the addition of the experimental condenser and the headphones in the one, the oscillator circuits are the same. The circuit constants of both circuits are also identical.

The oscillators were constructed on wood baseboards, using heavy copper for the panels. The batteries were also mounted directly on the baseboard. The receiving oscillator was shielded except for the bottom, the transmitting oscillator was not shielded. All wiring was done with number 14 copper wire, leads were made short and direct. The construction was made as rigid as possible mechanically in order to prevent any possible change in frequency due to vibration of the wiring or parts. The coils were covered with bakelite varnish and mounted solidly on stand-off insulators.

Both coils, L_1 and L_2 , were wound on the same form, three inches in diameter, and made of bakelite. The coils were close wound with about one-half inch of space between them and both were wound in the same direction. This precaution is necessary in order to insure oscillation. Another precaution necessary to insure oscillation was to connect the outside terminal of L_1 to the grid and the outside of L_2 to the plate. No trouble was experienced making



C_1 - 0.00035 mfd.

C_2 - 0.0001 mfd.

T - type 30 tube

R_1 - 100,000 ohms

R_2 - 30 ohms

S, S - toggle switches

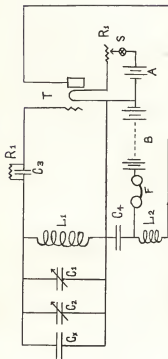
A - 3 volt A battery

B - 45 volt B battery

L_1 - 55 turns No. 22 d.c.c. on 3 inch coil form

L_2 - 44 turns No. 22 d.c.c. on 3 inch coil form

Fig. 1. Transmitting oscillator.



C_1 - 0.00010 mfd.

C_2 - 0.00008 mfd.

C_3 - 0.00025 mfd.

C_4 - 0.001 mfd.

C_x - Experimental condenser (see text)

T - type 30 tube

R_1 - 100,000 ohms

R_2 - 30 ohms

S - toggle switch

A - 30 volt A battery

B - 45 volt B battery

F - headphones

Fig. 2. Receiving oscillator.

these circuits oscillate. The type 30 tube required only 45 volts of B-battery in order to oscillate in this type of circuit. After the coils had been wound and tested they were given two coats of bakelite varnish to make them rigid and to prevent their being affected by any change in the moisture content of the air.

The small condenser, C_2 , of the receiving oscillator, is equipped with a National Vernier dial capable of reading tenths of dial divisions. This reading is necessary in order to measure the small differences in capacity at the surface of the liquid in the experimental condenser. Condenser C_1 of the receiving oscillator was not equipped with such a dial because it was not used for the measurements at the liquid surface but was used merely to tune the transmitting oscillator to a point where it would oscillate best.

The experimental condenser, C_x , of the receiving oscillator, was made from a piece of plate glass. The glass was covered with tinfoil and the tinfoil smoothed out and cemented in place with shellac, thinned with a little alcohol. For a support three set screws were soldered to pieces of copper bent in the shape of an inverted U. These copper pieces were then cemented to the upper side of the

plate glass. This arrangement made it easy to level the plate over the liquid and also to lower the plate to bring it closer to the liquid. Very small copper projections were also cemented to the plate in such a way that they would not come in contact with the tinfoil but would serve as a means of measuring the distance to the liquid surface. This made it possible to remove the plate, change the liquid, and then set the plate in the same position, relative to the liquid surface, as before.

The liquid itself acted as the lower plate of the condenser. This was placed in a pyrex dish. Contact was made to the liquid through an electrode made of nichrome wire sealed in a glass tube. Even with the use of conductivity water, it was found that the liquid acted as the lower surface and a submerged metal plate showed no effect on the capacity of the condenser until it was brought very near the surface.

EXPERIMENTAL

After the apparatus had been constructed and tested for oscillation the next step was that of calibration. The condensers in the receiving oscillator were calibrated for capacity and the transmitting oscillator was calibrated for

frequency range.

The calibration of the condensers was done with the aid of a General Electric capacity bridge. The calibration curves of condensers C_1 and C_2 are shown in figures 3 and 4 respectively. Condenser C_1 was not a straight line capacity condenser, as a result the calibration of capacity against dial reading does not show a straight line. The calibration curve of C_2 is a straight line. Condenser C_2 is the condenser that was used for all determinations of changes in capacity. The usual precaution of reversing the leads to the condenser from the bridge was taken in order to take in account any possible capacitance effects between the leads. After the curve had been drawn for C_2 the change in capacity per dial division was calculated and this factor was then used in determining capacity changes in later experiments.

The transmitting oscillator was calibrated for frequency range with a General Electric wavemeter. This was done only so that a frequency could be used which could not possibly interfere with any receivers in the neighborhood. The frequency plotted against the dial readings is shown in figure 5.

After the apparatus had been calibrated trials were

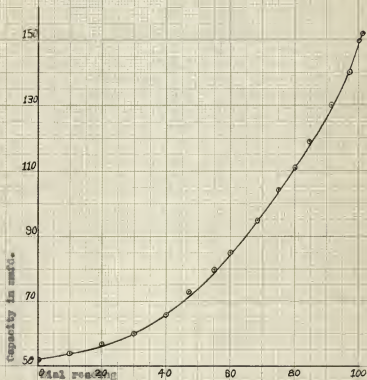
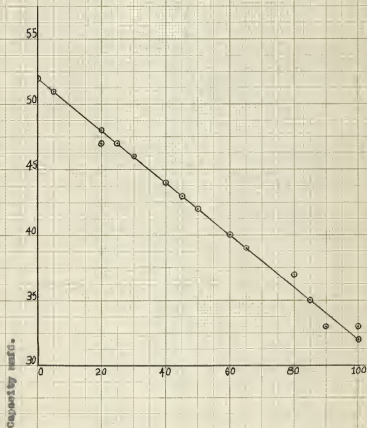


Fig. 8. Calibration of G_1 (G_2 set at 0)



Dial reading

Fig. 4. Calibration of C_2 (C_1 set at 0)

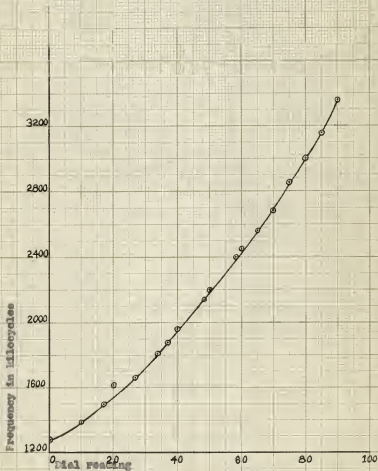


Fig. 8. Calibration of the transmitting oscillator in kilocycles.

made with distilled water to determine if the plate of the experimental condenser could be removed and then replaced without disturbing the setting of the condenser. This was found possible within 0.1 dial division. Further checks were made to see if liquid could be removed and then replaced with no change in readings. This was also found possible within plus or minus 0.1 dial divisions.

The plate of the experimental condenser was always set within 1 mm. of the liquid. This was possible by first placing the plate over the liquid and then gradually lowering it in place by adjusting the set screws. The points that were cemented in place on the condenser plate served as a means of regulating the distance above the surface for a series of successive readings.

Several different materials were then placed on distilled water, by means of a glass rod, and the changes in capacity determined. These materials included oleic acid, benzaldehyde, palmitic acid, stearic acid, mineral oil, o, m and p dinitrobenzene and p-nitrophenol. Palmitic and stearic acid, mineral oil and the dinitrobenzenes were first dissolved in benzene in order to allow them to spread over the surface.

Oleic acid was then placed over a weak salt solution

and capacitance changes noted. Oleic acid was also tried on weak solutions of $\text{Ca}(\text{OH})_2$ and NaOH of approximately the same normality.

Other capacitance effects noted and checked during the course of the experiments included: the effect of a submerged copper plate on the capacity of the experimental condenser, the effect of ripples on the surface of the solution, the condensation of vapor on the plate of the experimental condenser, the effect of solutions of electrolytes, the effect of changing leads to the experimental condenser, the rate of diffusion of a drop of salt solution, the rate of spreading of oleic acid and the effect of adding more surface active material after a monomolecular layer had already been placed on the surface.

During the course of all experimental work special precautions were taken to use pure materials and to keep the surfaces free of contamination while readings were being taken. All pieces of apparatus coming in contact with the liquid were carefully cleaned after each trial.

RESULTS

From the calibration of condenser C_2 , (figure 4), the change in capacity per dial division may be calculated, the change being 0.8 mmfd per division. This is the factor used in all calculations in the following tables. It will be noticed that a ratio between the total capacity and the change in capacity has been given in each case. This has been done in order for us to have a basis of comparison for the data in the different trials.

As has been suggested previously, several blank trials were made, removing the condenser plate and then replacing it. Six trials were made; three showed a change of 0.1 dial division, the other three showed no change.

Next, the plate was left in place and the liquid removed from the pyrex tray with a siphon. The liquid was then replaced, being measured each time with a volumetric flask. Six trials were made in this case, two showed a change of 0.1 dial division while the other four showed no change.

These data indicate a very slight tendency towards greater accuracy when the plate is left untouched and the

liquid removed. This is not possible, however, when a film has been deposited because it is necessary to clean the dish and the nichrome electrode after each trial.

The first readings taken were of oleic acid spread on distilled water. The results are shown in table 1. Several trials were also made on conductivity water. The results were the same as on distilled water. Tap water was also used as the liquid. In this case the results varied a great deal, indicating changes due to the salts in the water. Distilled water, therefore, was used in all cases.

Table 1. Change in capacity caused by oleic acid on distilled water.
Total C = 42 mmfd.

:Oleic			$\frac{\Delta C}{C}$: Deviations
Zero	Added	Diff. : (ΔC) :				: from mean
46.8	47.0	0.2	0.04	0.00095	0.00051	
48.1	48.4	0.3	0.06	0.00143	0.00003	
50.4	50.7	0.3	0.06	0.00143	0.00003	
46.5	46.9	0.4	0.08	0.00190	0.00044	
54.0	54.3	0.3	0.06	0.00143	0.00003	
50.0	50.4	0.4	0.08	0.00190	0.00044	
47.2	47.5	0.3	0.06	0.00143	0.00003	
48.9	49.3	0.4	0.08	0.00190	0.00044	
46.7	46.0	0.3	0.06	0.00143	0.00003	
48.8	50.0	0.2	0.04	0.00095	0.00051	
50.3	50.6	0.3	0.06	0.00143	0.00003	
46.9	47.2	0.3	0.06	0.00143	0.00003	
ΔC						
Av. C	0.00146					
Av. dev.	0.00021					
Extreme dev.	0.00051					

Tables 2 and 3 show the results of spreading oleic acid on an NaCl solution. These readings were taken in an effort to determine if any of the capacity changes noted on distilled water were due to increased conductivity of the water, the theory being that the ionization of the NaCl would effectively cover any slight ionization of the oleic acid. The results are the same as on distilled water, indicating that the results are not due to such effects. The solution had to be very dilute in order for the apparatus to oscillate. When the capacity became too great the receiver went out of oscillation.

Table 2. Change in capacity caused by oleic acid on a dilute NaCl solution.

Conditions: NaCl (concn. 0.04 gm/l)

Total C = 45 mmfd.

Zero	Oleic added	Diff.	(ΔC)	$\frac{\Delta C}{C}$	Deviations
60.2	60.5	0.3	0.06	0.00135	0.00008
61.4	61.7	0.3	0.06	0.00135	0.00008
60.7	61.1	0.4	0.08	0.00178	0.00051
59.8	60.0	0.2	0.04	0.00089	0.00038
59.9	60.1	0.2	0.04	0.00089	0.00038
59.8	60.1	0.3	0.06	0.00135	0.00008
Av. $\frac{\Delta C}{C}$		0.00127			
Av. dev.		0.00025			
Extreme dev.		0.00061			

Table 3. Change in capacity caused by oleic acid on a dilute NaCl solution.
 Conditions: NaCl (concn. 0.08 gm/l)
 Total C = 43 mmfd.

Zero	oleic added	Diff. :	(ΔC) :	$\frac{\Delta C}{C}$	Deviations
52.9	53.2	0.3	0.06	0.00139	0.00008
54.3	54.4	0.1	0.02	0.00047	0.00004
54.8	55.1	0.3	0.06	0.00139	0.00008
48.9	49.3	0.4	0.08	0.00186	0.00055
48.4	48.7	0.3	0.06	0.00139	0.00008
52.7	53.0	0.3	0.06	0.00139	0.00008
Av. $\frac{\Delta C}{C}$	0.00151				
Av. dev.	0.00008				
Extreme dev.	0.00004				

Table 4 also gives indication of the changes in capacity being due to the electric moment of the molecule rather than any ionisation or dissolving of the acid. In this case a drop of oleic acid was placed on the surface of distilled water and the reading taken, then another drop was placed on the surface. There was no further change in capacity. It appears that the film formed with the first drop covered the entire tray and that equilibrium had been established between the film and the water. If there had been any possible changes due to the acid's dissolving or ionizing in the water it seems likely that

further addition of oleic acid would have caused further changes in capacity. Such was not the case.

Table 4. Change in capacity due to a second drop of oleic acid.

Zero	First drop of acid	Diff.: (ΔC)	Second drop of acid	Further change in C
46.8	47.0	0.2	0.04	47.0 : 0.00
48.1	48.4	0.3	0.06	48.4 : 0.00
50.4	50.7	0.3	0.03	50.7 : 0.00
45.5	45.9	0.4	0.03	45.9 : 0.00
54.0	54.3	0.3	0.06	54.3 : 0.00

Next oleic acid was placed on the surface of an 0.0021 N $\text{Ca}(\text{OH})_2$ solution. The $\text{Ca}(\text{OH})_2$ was titrated with a standard acid solution to determine its normality. The capacity changes in this case were much greater than those found for oleic acid on distilled water, or on a salt solution. Blodgett (1935) found, when collecting films of long chain fatty acids on alkaline solutions, that the salt of the acid was actually deposited, rather than the acid itself. Thus it appears probable that in this case calcium oleate was formed. The results being what they are (about eight times as great as on distilled water) would lead us to believe that such is the case.

Another interesting feature of the work with the $\text{Ca}(\text{OH})_2$ solution was the noticeable change in beat note

caused by the formation of calcium carbonate at the surface of the liquid. This caused a gradual decrease in the capacity of the experimental condenser. The explanation very likely would be that as the calcium carbonate was being formed ions were being taken from the liquid. Thus the conductivity of the liquid decreased and as a result the capacity of the condenser also decreased. It was found that by blowing across the liquid the rate of change of the heat note could be increased.

Table 5. Change in capacity of oleic acid on a weak Ca(OH)_2 solution.
Conditions: soln. 0.0021 N Ca(OH)_2
Total C = 85 mmfd.

Zero	oleic added	Diff. : (ΔC) :	$\frac{\Delta C}{T}$	Deviations
40.8	43.3	2.5	0.56 : 0.0066	0.0020
46.3	51.2	4.9	0.98 : 0.0118	0.0029
51.0	54.7	3.7	0.74 : 0.0087	0.0001
48.8	52.9	4.1	0.82 : 0.0096	0.0011
52.5	55.0	2.5	0.50 : 0.0059	0.0017
47.7	50.8	3.1	0.62 : 0.0073	0.0013
52.2	56.0	3.8	0.76 : 0.0087	0.0021
46.0	50.4	4.4	0.88 : 0.0104	0.0018
Av. $\frac{\Delta C}{C}$		0.0066		
Av. dev.		0.0016		
Extreme dev.		0.0029		

An NaOH solution, of approximately the same normality as the Ca(OH)_2 , was prepared next. This solution, when

titrated, showed a normality of 0.0018. Oleic acid was placed on this solution. The results indicate a change in capacity about three-fourths as great as in the case of the $\text{Ca}(\text{OH})_2$. It is very likely that the sodium salt of oleic acid is formed in this case. It would appear, however, that the change in capacity should be at least as great as in the case of the $\text{Ca}(\text{OH})_2$ solution. The difference is probably found in the different solubilities of the calcium and sodium oleate, the sodium oleate being the more soluble. It is likely that the polar group of the sodium oleate would therefore pull the molecule that much farther into the liquid and by doing so, remove the charge that much farther from the condenser plate.

The solubility theory is further strengthened by a noticeable effect in the beat note after the oleic acid has been added. The beat note rapidly approached a maximum and then started a gradual decrease in value, indicating a possible removal of the molecules from the vicinity of the surface of the solution where they would, of course, have a greater effect on the capacity of the condenser.

Table 6. Change in capacity of oleic acid on a weak NaOH solution.

Conditions: soln. 0.0018 N NaOH

Total C = 42 mmfd.

Zero	Added	Diff.	(ΔC)	$\frac{\Delta C}{C}$	Deviations
49.9	51.4	1.5	0.30	0.0071	0.0007
49.6	50.7	1.1	0.22	0.0052	0.0012
46.3	46.7	1.4	0.28	0.0066	0.0002
49.7	51.4	1.7	0.34	0.0081	0.0017
55.0	54.0	1.0	0.20	0.0049	0.0024
51.2	52.5	1.3	0.26	0.0065	0.0001
Av. $\frac{\Delta C}{C}$	0.0064				
Av. dev.	0.0010				
Extreme dev.	0.0024				

Another material checked on distilled water was benzaldehyde. Benzaldehyde has an electric moment of approximately the same value as oleic acid. The change in capacity was approximately the same.

An effect noticeable in the case of benzaldehyde was a decrease in the beat note soon after reaching a peak. This effect may be due to two causes. First, benzaldehyde has a fairly high vapor pressure and it may have evaporated rather rapidly, second, it may have been oxidized into benzoic acid and dissolved into the liquid. The results are shown in the following table.

Table 7. Change in capacity due to benzaldehyde on distilled water.
Total C = 45 mmfd.

Zero	:Benzaldehyde : added	: Diff.:	(ΔC) :	$\frac{\Delta C}{C}$:Deviations
54.0	: 54.3	: 0.3	: 0.06	: 0.00199	: 0.00006
50.1	: 50.3	: 0.2	: 0.04	: 0.00093	: 0.00052
50.9	: 51.1	: 0.2	: 0.04	: 0.00093	: 0.00052
48.4	: 48.6	: 0.2	: 0.04	: 0.00093	: 0.00052
49.8	: 50.3	: 0.5	: 0.10	: 0.00237	: 0.00092
50.4	: 50.8	: 0.4	: 0.08	: 0.00190	: 0.00045
49.4	: 49.7	: 0.3	: 0.06	: 0.00199	: 0.00006
50.2	: 50.6	: 0.4	: 0.08	: 0.00190	: 0.00045
48.7	: 49.1	: 0.4	: 0.08	: 0.00190	: 0.00045
51.3	: 51.6	: 0.3	: 0.06	: 0.00199	: 0.00006
50.6	: 50.8	: 0.2	: 0.04	: 0.00093	: 0.00052
Av. $\frac{\Delta C}{C}$	0.00145				
Av. dev.	0.00041				
Extreme dev.	0.00092				

Palmitic and stearic acids, and mineral oil were also placed on a distilled water surface. All three materials were dissolved in benzene in order to give them a medium for spreading. The effects of mineral oil and palmitic acids were zero. Stearic acid showed a very slight change in beat note, but not enough to measure.

The results can probably be explained by a comparison of their electric moments with that of other materials measured. In the case of mineral oil the electric moment is zero. The electric moments of the long chain fatty acids as determined by Schulman and Rideal (1930) have

values approximately one-tenth as great as oleic acid and benzaldehyde, a value, which, if we are correct in assuming the electric moment to cause the change in capacity, would be beyond the limits of sensitivity of the apparatus used.

Five trials were made with mineral oil and six each were made on palmitic and stearic acids.

The next material tested was p-nitrophenol, a compound which, according to Smyth (1931), has an electric moment of 5.0×10^{-18} e.s.u. This material, however, is slightly soluble. The results, when it was placed on distilled water, from a benzene solution, are shown in table 8.

Table 8. Change in capacity due to p-nitrophenol on distilled water.
Total C = 42 mmfd.

p-nitrophenol		Diff.	:	(ΔC) :	$\frac{\Delta C}{C}$: Deviations
Zero	added					
47.3	48.0	0.7	:	0.14	0.00333	0.00012
51.0	51.8	0.8	:	0.16	0.00381	0.00060
49.8	50.3	0.7	:	0.14	0.00333	0.00012
49.5	50.1	0.6	:	0.12	0.00286	0.00036
50.4	51.1	0.7	:	0.14	0.00333	0.00012
48.2	48.8	0.6	:	0.12	0.00286	0.00036
50.7	51.4	0.7	:	0.14	0.00333	0.00012
49.9	50.5	0.6	:	0.12	0.00286	0.00036
Av. $\frac{\Delta C}{C}$		0.00321				
Av. dev.		0.00027				
Extreme dev.		0.00060				

It was thought that some of the change in capacity noted must have been due to its solubility in the water. In order to obtain a check on this theory the p-nitrophenol was placed on a salt solution. The change in capacity in this case was not as large as in the case of the distilled water solution. The results seem to indicate that the solubilities of materials have a decided effect on capacitance changes.

Table 9. Change in capacity due to p-nitrophenol on a weak NaCl solution.

concn. NaCl 0.04g/l

Total C = 60 mmfd.

Zero	: p-nitrophenol added	: Diff.	: (ΔC)	: $\frac{\Delta C}{C}$: Deviations
68.8	: 70.0	: 0.2	: 0.04	: 0.00067	: 0.00006
66.5	: 66.6	: 0.1	: 0.06	: 0.00100	: 0.00029
59.9	: 60.2	: 0.3	: 0.06	: 0.00100	: 0.00029
61.5	: 61.5	: 0.0	: 0.04	: 0.00067	: 0.00006
60.5	: 60.6	: 0.1	: 0.02	: 0.00033	: 0.00037
67.6	: 67.8	: 0.2	: 0.04	: 0.00067	: 0.00006
66.5	: 66.6	: 0.1	: 0.04	: 0.00067	: 0.00006
Av. $\frac{\Delta C}{C}$		0.00071			
Av. dev.		0.00016			
Extreme dev.		0.00037			

In order to obtain a check of some kind on materials having approximately the same structure, but having different electric moments, o-, m- and p-dinitrobenzene were all tested on distilled water.

The results on o-dinitrobenzene are shown in table 10.

The changes in capacity were fairly constant for all trials. The dinitrobenzene was spread from a benzene solution and the result of adding more than two drops of solution was also checked in this case. There was no further change in capacity noted. After the benzene had evaporated, the o-dinitrobenzene was left on the surface in small groups of crystals, indicating that equilibrium with the water had been established before the further addition of the dinitrobenzene.

Table 10. Change in capacity due to o-dinitrobenzene on distilled water.
Total C = 42 mmfd.

Zero	o-dinitrobenzene added	Diff.	(ΔC)	$\frac{\Delta C}{C}$	Deviations
50.2	50.6	0.4	0.08	0.00190	0.00000
51.7	52.0	0.3	0.06	0.00143	0.00047
56.1	56.5	0.4	0.08	0.00190	0.00000
55.1	55.6	0.5	0.10	0.00238	0.00048
49.4	49.8	0.4	0.08	0.00190	0.00000
48.8	49.1	0.3	0.06	0.00143	0.00047
50.3	50.7	0.4	0.08	0.00190	0.00000
51.1	51.6	0.5	0.10	0.00238	0.00048
53.3	53.7	0.4	0.08	0.00190	0.00000
48.6	49.0	0.4	0.08	0.00190	0.00000
Av. $\frac{\Delta C}{C}$	0.00190				
Av. dev.	0.00019				
Extreme dev.	0.00048				

m-dinitrobenzene was the next material tested. The changes in capacity noted in this case were almost as large as in the case of the ortho compound. It would seem, accord-

ing to the electric moments of the two materials, that the change in capacity of the meta compound would only be about one-half that of the ortho compound. However, the *m*-dinitrobenzene is more soluble in water than the *o*-dinitrobenzene. It may be that the increased conductivity due to this difference in solubility may have caused the change to be as large as in the case of *o*-dinitrobenzene.

Another explanation may be possible. Both these compounds orient themselves on the surface in much the same manner, that is, with the benzene ring vertical, or nearly so. This would mean that in each case, the area occupied per molecule would be about the same. Then we would have just as many electrical charges in a given area, in each case. It may be that the number of electrical charges present is affecting the capacity of the condenser fully as much as the electric moment itself.

Table 11. Change in capacity due to m-dinitrobenzene on distilled water.
Total C = 44 mmfd.

Zero	m-dinitrobenzene added	Diff.	(ΔC)	$\frac{\Delta C}{C}$	Deviations
52.9	53.2	0.4	0.08	0.00181	0.00015
45.7	46.2	0.5	0.10	0.00223	0.00032
58.0	58.3	0.3	0.06	0.00136	0.00030
56.8	57.2	0.4	0.08	0.00181	0.00015
46.9	46.2	0.3	0.06	0.00136	0.00030
58.5	58.9	0.4	0.08	0.00181	0.00015
52.1	52.4	0.3	0.06	0.00136	0.00030
54.7	55.0	0.3	0.06	0.00136	0.00030
52.3	52.7	0.4	0.08	0.00181	0.00015
Av. $\frac{\Delta C}{C}$	0.00166				
Av. dev.	0.00027				
Extreme dev.	0.00062				

The last of this series of compounds, p-dinitrobenzene, was tested next. With this material, a series of determinations, showed very little change in capacity. A slight change in beat note was heard, but it was too small a change to measure. The position of the NO_2 groups is such that the electric moment is zero. It also causes the molecule to lie flat on the surface of the water. Both of these factors probably contribute to effect noted.

Table 12. Change in capacity due to p-dinitrobenzene on distilled water.
Total C = 42 mmfC.

Zero	p-dinitroben- zene added	: Diff. :	(ΔC):
48.8	48.8	: 0.0 :	0.00
49.1	49.1	: 0.0 :	0.00
47.8	47.8	: 0.0 :	0.00
48.8	48.8	: 0.0 :	0.00
48.9	48.9	: 0.0 :	0.00
49.2	49.2	: 0.0 :	0.00
48.5	48.5	: 0.0 :	0.00
48.8	48.9	: 0.1 :	0.02
50.1	50.1	: 0.0 :	0.00
49.9	49.9	: 0.0 :	0.00
48.8	48.9	: 0.1 :	0.02
47.7	47.8	: 0.1 :	0.02
46.3	46.3	: 0.0 :	0.00
45.9	45.9	: 0.0 :	0.00

Because m-dinitrobenzene was slightly soluble it was dissolved in distilled water to make a saturated solution. This solution was then placed in the pyrex dish, the condenser plate lowered in place, and the reading taken. The solution was then diluted one-half and another reading taken and any change in capacity from that of the saturated solution noted. It will be recalled that removing solution and then replacing it could be done with little error. It is therefore probable that the few slight changes noted were due to experimental error.

Next the solution was diluted to a proportion of one to four and the total change in capacity again noted.

Finally, distilled water was placed in the dish and the reading taken. The total change in capacity from the saturated solution to the distilled water is shown. These changes are of the same order as those obtained by placing the *m*-dinitrobenzene on the water from the benzene solution. Evidently equilibrium had been established in the case of the benzene solution. The results are shown in the following table.

Table 13. Change in capacity of a saturated solution of *m*-dinitrobenzene when diluted with distilled water.

Zero	:Diluted			:Diluted			:Distilled		
	: 1-2	: ΔC		: 1-4	: ΔC		: water	: ΔC	
47.7	: 47.7	: 0.0	:	47.5	: 0.2	:	47.4	: 0.3	
49.9	: 49.9	: 0.0	:	49.6	: 0.3	:	49.5	: 0.4	
50.4	: 50.3	: 0.1	:	50.1	: 0.3	:	50.0	: 0.4	
51.9	: 51.8	: 0.1	:	51.7	: 0.2	:	51.6	: 0.3	
46.6	: 46.6	: 0.0	:	46.4	: 0.2	:	46.3	: 0.3	
48.8	: 48.7	: 0.1	:	48.5	: 0.3	:	48.4	: 0.4	
54.4	: 54.4	: 0.0	:	54.2	: 0.2	:	54.2	: 0.2	
57.1	: 57.1	: 0.0	:	56.9	: 0.2	:	56.8	: 0.3	

In table 14 an attempt has been made to determine how much of the capacity changes noted were due to an increased conductivity of the distilled water when a material was placed on the surface. This table shows the effect of a saturated solution of the surface active material as compared with distilled water. In order to make these readings a conductivity cell was connected to the receiving

oscillator in place of the experimental condenser. Changes in capacity were then noted for the different saturated solutions as compared with distilled water.

These changes are much more sensitive than would be the case with the experimental condenser. In this case, both plates were submerged in the liquid. In the experimental condenser there is an air gap of about 1 mm between the liquid surface and the upper plate. These readings cannot then be used quantitatively but do give us an indication of the materials which were affected by such changes in capacity.

Table 14. Change in capacitance due to solubility of surface active material.

H ₂ O reading:	Material added:	Reading :	ΔC
21.3	: Oleic acid	: 21.3	: 0.0
		: 21.3	: 0.0
		: 21.4	: 0.1
		: 21.3	: 0.0
		: 21.1	: -0.2
		: 21.0	: -0.3
21.3	: Palmitic acid	: 21.3	: 0.0
		: 21.4	: 0.1
		: 21.4	: 0.1
		: 21.3	: 0.0
		: 21.3	: 0.0
		: 21.2	: -0.1
21.3	: Stearic acid	: 21.1	: -0.2
		: 21.3	: 0.0
		: 21.4	: 0.1
		: 21.4	: 0.1
		: 21.3	: 0.0
		: 21.0	: -0.3
21.6	: Benzaldehyde	: 21.8	: 0.3
		: 21.6	: 0.1
		: 21.9	: 0.4
		: 22.0	: 0.5
		: 21.6	: 0.3
21.6	: p-nitrophenol	: 22.1	: 0.6
		: 22.0	: 0.5
		: 22.2	: 0.7
		: 21.9	: 0.4
		: 22.2	: 0.6

Table 14. Continued.

H_2O readings:		Material added:	Reading :	ΔC
21.6	<i>iso</i> -dinitrobenzene	:	21.6	0.0
		:	21.5	-0.1
		:	21.8	0.2
		:	21.6	0.0
		:	21.7	0.1
21.6	<i>m</i> -dinitrobenzene	:	21.8	0.2
		:	21.9	0.3
		:	21.7	0.1
		:	21.9	0.3
		:	21.9	0.2
21.6	<i>sp</i> -dinitrobenzene	:	21.6	0.0
		:	21.4	-0.2
		:	21.9	0.3
		:	21.7	0.1
		:	21.6	0.0
		:	21.7	0.1

Tables 15, 16 and 17 present data on other effects noted during the course of the experimental work. We were interested in knowing the effect of a submerged plate upon the capacitance of the experimental condenser. A copper plate was placed in the bottom of the dish and contact made to it rather than to the liquid itself. The results clearly show that this submerged plate has no effect upon the total capacity of the experimental condenser. The liquid surface, then, must act as the lower plate of the condenser.

It was noticed that oleic acid, when spread on water, did not reach equilibrium at once. This effect may be due

to the time needed for the acid to spread. It would be interesting to note such time effects with other insoluble materials as compared with their spreading coefficients. Time has not permitted any further investigation of such effects.

When a material, such as salt, is placed in a solution, the capacity immediately increases, changing at a rather steady rate. This effect was also timed. One drop of salt solution was placed on the distilled water and the time necessary to reach equilibrium was determined. This does not necessarily mean that diffusion is complete in this length of time. It simply indicates that the diffusion had progressed far enough so that any further diffusion had no noticeable effect on the capacity of the interfacial condenser.

Table 15. Effect of a submerged plate on capacity.

Plate out	:	Plate in	:	Change
49.8	:	49.7	:	0.1
49.9	:	50.0	:	0.1
49.5	:	49.5	:	0.0
49.6	:	49.6	:	0.0
49.3	:	49.3	:	0.0
50.6	:	50.7	:	0.1

Table 16. Time for the change in capacity due to oleic acid to become constant.

Zero	Oleic	Change	Time(seconds)
46.8	47.0	0.2	6
48.1	48.4	0.3	7
50.4	50.7	0.3	6
45.5	45.9	0.4	6
54.0	54.3	0.3	7

Table 17. Time for the capacity change to become constant in the case of electrolytes.

Zero	NaCl added	Change	Time(minutes & seconds)
48.8	50.9	1.1	8:30
50.3	51.7	1.4	9:00
48.6	49.1	1.5	9:15
53.2	54.4	1.2	8:50
49.9	51.2	1.3	8:45

Table 18 attempts to combine all the data obtained into one convenient form. The electric moments of the materials investigated are also shown. The data given are the averages of the several trials together with the average deviations.

The results indicate that $\Delta C/C$, the change in capacity divided by the total capacity, bears some definite relation to the electric moment.

Table 18. Average results compared with the electric moments.

Material	Substrate	ΔC C	Electric moments $\times 10^{-18}$
Oleic acid	distilled H_2O	0.00146 ± 21	2.5 (1)
Oleic acid	$NaCl(0.04g/l)$	0.00127 ± 25	:
Oleic acid	$NaCl(0.08g/l)$	0.00131 ± 28	:
Oleic acid	$Ca(OH)_2(0.0021M)$	0.00850 ± 160	:
Oleic acid	$NaOH(0.0018M)$	0.00640 ± 100	:
Benzaldehyde	distilled H_2O	0.00145 ± 41	2.75 (2)
Palmitic acid	distilled H_2O	0.00000	0.25 (3)
Stearic acid	distilled H_2O	0.00000	0.25 (3)
Mineral oil	distilled H_2O	0.00000	0.00
p-nitrophenol	distilled H_2O	0.00321 ± 27	5.00 (2)
p-nitrophenol	$NaCl(0.04g/l)$	0.00071 ± 16	:
o-dinitrobenzene	distilled H_2O	0.00190 ± 19	6.00 (4)
m-dinitrobenzene	distilled H_2O	0.00166 ± 27	3.70 (4)
p-dinitrobenzene	distilled H_2O	0.00000	0.00 (4)

(1) Guastalla and Perrin(1933)

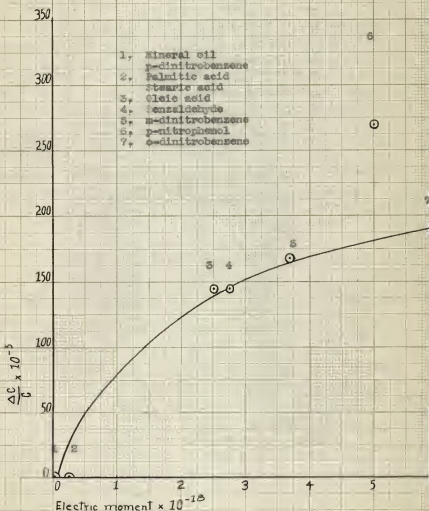
(2) Smyth (1931)

(3) Schulman and Rideal (1930)

(4) Williams (1930)

The relationship between $\Delta C/C$ may be seen to even better advantage in figure 6.

There is considerable discrepancy in some of the results. These are likely due to the several factors mentioned before that affected the capacity of the condenser along with the electric moment. It is very likely that



Electric moment $\times 10^{-18}$

Fig. 6. Relation of $\frac{\Delta C}{C}$ to the electric moment

these factors appear in the graph. The data shown in the graph are those taken on a distilled water surface. The data on the p-nitrophenol show that a great deal of the change noted was due to the solubility of the material. Even with these factors present, it appears, from the limited data presented, that the electric moment has a very definite influence upon the changes in capacity, as determined by the method described in this paper.

CONCLUSIONS

1. The electric moment in a monomolecular film spread on water affects the capacity of an interfacial condenser.
2. The heterodyne beat method may be used to determine such changes in capacity.
3. Other factors, such as ionization, solubility, diffusion, condensation of vapor, evaporation, and accidental contamination, also affect the capacity of the interfacial condenser.
4. In order to make an accurate, quantitative study of the surface effects, the factors mentioned in 3 would have to be accurately controlled.
5. Other effects capable of being detected by such a method include: rate of formation of a precipitate, the

rate of diffusion of an electrolyte through the solution and rate of spreading of a surface active material.

6. It appears likely that the electric moment of the molecule, its surface orientation, and its size should affect the capacity of the condenser.

7. It is probable, that a method such as described, could be refined to the point at which the electric charges of molecules could be quantitatively studied. This study would call for a precise control of the several factors that appear to affect the capacity of the interfacial condenser.

SUMMARY

An apparatus, consisting of two radio frequency oscillators, was constructed. These were arranged so that any changes in capacity at an experimental condenser could be detected. The experimental condenser consisted of a glass plate covered with tinfoil and arranged so that it could be lowered near the liquid surface. The liquid acted as the lower plate of the condenser. The apparatus was then used to determine changes in capacity due to monomolecular films on liquid surfaces.

The method of noting changes in capacity was the famil-

lar heterodyne beat method. Changes in capacity of the order of 0.2 mufds. could be detected.

The changes in capacity due to films of oleic acid, palmitic acid, stearic acid, mineral oil, benzaldehyde, p-nitrophenol and o-, m- and p-dinitrobenzene were determined.

Water was the common liquid medium used although oleic acid was placed on NaCl solution and also weak solutions of NaOH and $\text{Ca}(\text{OH})_2$. P-nitrophenol was also checked on a weak solution.

Variable factors were controlled as nearly as possible. Some of these factors included solubility, evaporation, rate of spreading, rate of diffusion and condensation of vapors as well as some effects due to slight ionization of the materials.

The results indicate that a method such as described could, with certain refinements, be used to study quantitatively many of the electrical effects of liquid surfaces including the electric moment. The results given, although largely qualitative in nature, indicate quite positive changes in capacity due to the dipole moment of surface active films of monomolecular thickness.

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