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THE EFFECT OF A POTENTIAL ON INTERFACIAL SURFACE TENSION.

A THESIS

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INTRODUCTION.

The object of this work was to study the effect of a potential on liquid-liquid interfaces. Both the capillary and drop weight methods were used to note the change of interfacial tension produced by potentials ranging from seven and one half volts to several hundred thousand volts. This work is divided into three parts.

The first consists of a study of the effect of varying potentials on different concentrations of sodium oleate solution against benzene, mutually saturated with each other and measuring the change of interfacial tension thus produced.

The second part is a study of the behavior of different organic liquids against water, mutually saturated with each other, using voltages as high as several hundred thousand volts across the interface in the capillary.

The third part is a repetition of the first; the drop weight method being used instead of the capillary method. It was attempted to show that the mollecules of an emulsifying agent such as sodium oleate were reoriented 180° from their normal direction of orientation or the concentration of the soap mollecules in the interface is changed under the influence of a certain direction of potential. It was attempted to show that the interfacial surface tension was increased under the influence of a certain direction of potential and decreased when the potential was reversed. A study is also made of the influence of a potential on the speed of saturation of a second liquid such as water in a water-benzene system. This is shown by the difference of interfacial surface tension with and without a potential.

THE CAPILLARY METHOD WITH POTENTIALS RANGING FROM 7 1/2 TO 110 VOLTS.

BENZENE AGAINST SODIUM OLEATE SOLUTIONS.

DESCRIPTION OF APPARATUS AND MATERIALS:- The apparatus used in studying the effect of a potential on interfacial tension by the capillary method consisted of two large glass tubes, one long with a diameter of 2.12 cm., and a short one with a diameter of 2.03 cm., connected by a capillary of fairly constant bore. The capillary was in an upright position. When two fairly immiscible liquids were put in the system, the meniscus was brought somewhere near the center of the capillary. Through stoppers at the openings of the large tubes, adjustable platinum electrodes were placed.

Water or aqueous sodium oleate solution was placed in the long large tube and benzene in the short large tube with the meniscus in the capillary. Two motor generators, producing direct current, were used, the one producing a potential of 110 and 55 volts, the other producing a potential of 15 and 7 1/2 volts. A milliameter was placed in series with the capillary apparatus.

METHOD OF PROCEDURE:- The glass capillary apparatus was first thoroughly cleaned, -Hot cleaning solution was first forced through the capillary. It was then rinsed well and then steamed with live steam for some time and then dried.

The two liquids which were mutually saturated were then placed in the apparatus so that the meniscus between the two liquids was in the capillary. The electrodes were then placed in the two liquids. Because of the almost perfect non conducting liquid in the short large tube, the platinum electrode was brought close to the meniscus in the capillary and adjusted continually to keep a constant distance between the meniscus and the electrode.

Benzene and sodium oleate solution were used with a potential ranging from 7 1/2 volts to 110 volts.

CALCULATION OF INTERFACIAL TENSION BY THE CAPILLARY METHOD.

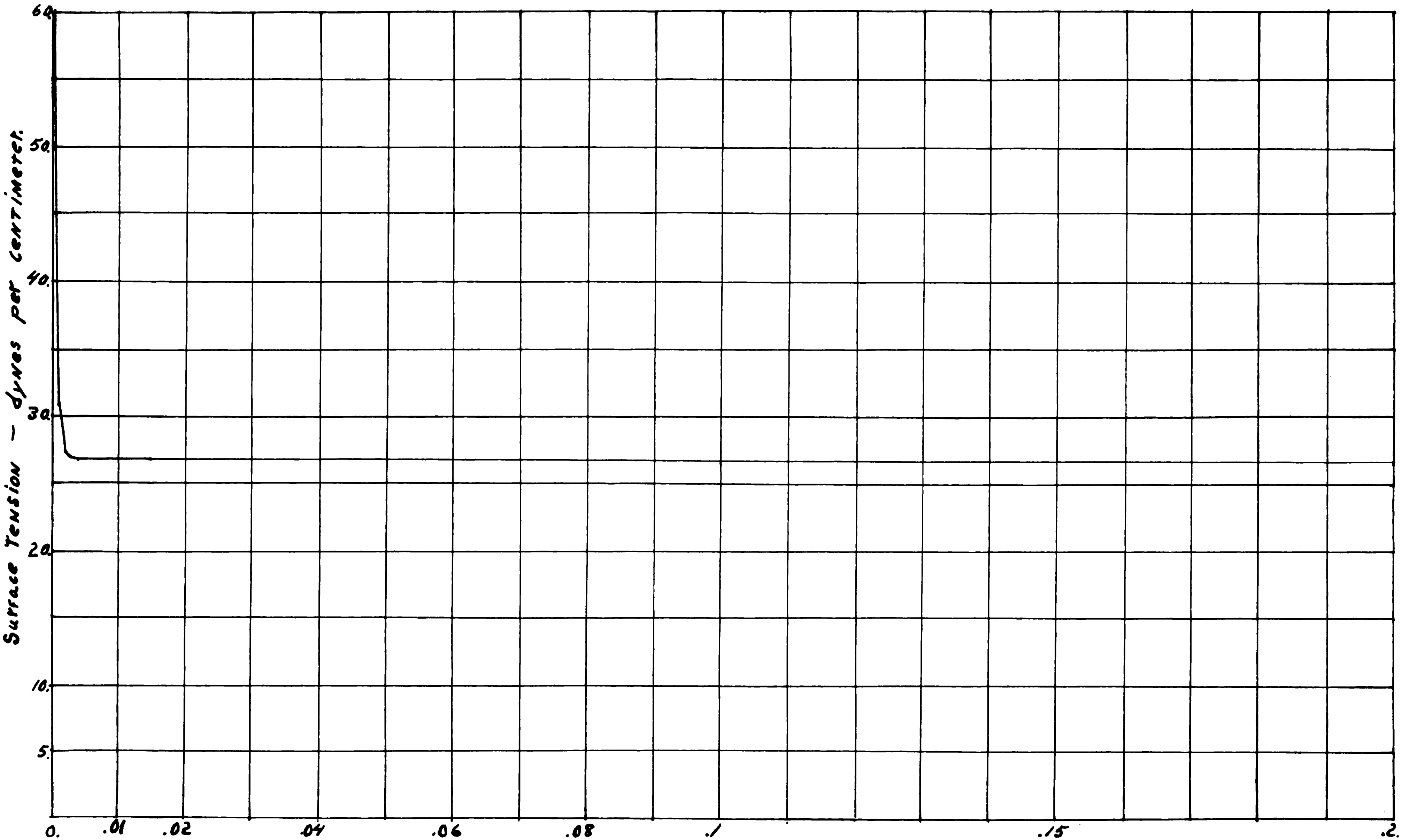
To calculate the correction of levels in the large tubes due to unequal surface tensions, the formula was used-

$$\frac{(\text{dynes/cm. of sol'n})(\ )(\text{Diameter})}{(\text{Density})(981)(\ )(r\ )} = H \qquad (1)$$

which reduces to the formula-

$$\frac{(\text{dynes/cm. of sol'n.})(2)}{(\text{density})(981)(\text{radius})} = H \qquad (2)$$

The static surface tension of aqueous solutions of sodium oleate saturated with benzene is found on graph (1), and may be substituted in formula (2), and the height (H_1) due to surface tension of the sodium oleate solution is found at 20° C. The height (H_2) of the benzene in the large tube



Percent Sodium Oleate in Water Saturated with benzene at 20° C. Fig. I.

due to surface tension of the benzene saturated with sodium oleate and water is found by substituting the value of the surface tension of benzene saturated with sodium oleate and water at 20 C., which is practically constant for all concentrations of sodium oleate at 23.33 dynes per cm.

To calculate the interfacial tension between the benzene and sodium oleate solution, let A equal the height of the benzene in the capillary apparatus above the meniscus in centimeters and B the height of the sodium oleate solution above the meniscus in centimeters, then;

$$(A-H_2)(0.879)\ (B-H_1)(1.0) = C$$

C is the height of a column of liquid with a specific gravity of 1.0 that is supported by the interfacial tension between the sodium oleate solution and benzene in the capillary, and;

$$\frac{(C)(\pi)(r^2)(981)}{(\pi)(D)} = \text{Interfacial tension in dynes/cm.}$$

(r) is the radius of the capillary (0.1403 cm.) and D the diameter of the capillary.

TABLE I.

0.05% Sodium Oleate Against Benzene.

Volts	Height of Benzene In Cm.	Height of Sodium Oleate Solution. In Cm.	Height of Meniscus In Cm.	Column of Water Supported by Interfacial Tension, Cm.	Interfacial Tension in Dynes/Cm.
0	12.07	11.03	6.19	0.330	22.85
15	-12.05	11.05	5.20	0.156	10.84
15	12.07	-11.03	6.30	0.357	24.27
0	11.92	10.81	5.50	0.325	22.37
55	-11.90	10.34	4.06	0.066	4.66
55	11.92	-10.81	5.72	0.362	25.10
0	12.60	11.49	6.18	0.317	21.92
110	-12.57	11.52	4.49	0.016	1.13
110	12.61	-11.48	6.43	0.362	25.10

TABLE II.

0.1% Sodium Oleate Against Benzene.

Volts	Height of Benzene In cm.	Height of Sodium Oleate Solution In Cm.	Height of Meniscus In Cm.	Column of Water Supported by Interfacial Tension, Cm.	Interfacial Tension In Dynes/Cm.
0.0	12.18	11.33	6.31	0.210	14.40
7.5	-12.17	11.34	6.50	0.155	10.46
7.5	12.18	-11.33	6.93	0.239	16.51
0.0	11.42	10.54	5.97	0.211	14.57
15.0	-11.41	10.55	5.28	0.0375	6.01
15.0	11.42	-10.54	6.24	0.265	18.17
0.0	11.16	10.15	4.57	0.207	14.23
55.0	-11.14	10.17	3.54	0.020	1.41
55.0	11.13	-10.13	5.26	0.333	22.95
110.0	13.76	12.63	6.13	0.210	14.36
110.0	-13.74	12.65	5.02	0.0015	0.083
110.0	13.78	-12.62	6.39	0.335	23.30

TABLE III.

0.5% Sodium Oleate Against Benzene.

Volts	Height of Benzene In Cm.	Height of Sodium Oleate Solution In Cm.	Height of Meniscus In Cm.	Column of Water Supported by Interfacial Tension, Cm.	Interfacial Tension In Dynes/Cm.
0	12.54	11.54	5.14	0.094	6.41
55	12.53	11.55	4.67	0.006	0.45
55	12.55	11.53	5.45	0.151	10.42
0	13.91	12.97	7.03	0.097	6.73
110	13.90	12.98	6.49	-0.0003	-0.017
110	13.92	12.96	7.53	1.920	13.63

DISCUSSION:- In all cases when the polarity of the sodium oleate solution was positive and the polarity of the benzene negative the interfacial tension was decreased and when the potential was reversed, the interfacial tension was increased. The explanation which immediately suggests itself, is that the concentration of the sodium oleate at the interface has changed or some of the mollecules in the interface have re-oriented themselves under the influence of the potential. The fact that the interfacial tension could never be lowered below zero (within experimental error) and could not be increased above the interfacial tension of water and benzene argues for the fact that this change of meniscus was due to a change of interfacial tension which was due to a change of interfacial tension which was due to a change of concentration or a reorientation of the mollecules of sodium oleate in the interface.

If we look upon the (-COONa) as the negative end of the soap mollecule and the long hydrocarbon chain as the positive end, we would expect when the polarity of the sodium oleate solution was positive and the benzene negative that the interfacial tension would be decreased as what was actually observed due to a higher concentration of sodium oleate mollecules in the interface due to the influence of the potential. It would also be expected that when the potential reversed that there would be a decrease in the concentration of the sodium oleate mollecules in the interface or a re-orientation of a part of the soap mollecules 180 from their original direction of orientation thus producing an increase in interfacial tension as what was actually observed. However, these results are contrary to the results obtained by the drop weight method where the sodium end of the soap mollecule acted as the positive end instead of the negative end.

One of the objections to the technique of this method is that when the platinum electrode in the benzene is very close to the meniscus but does not touch the thin film of sodium oleate solution which crawls up the capillary between the benzene and the glass, no results are obtained with a potential, or if the meniscus does change it is so small a change that it could not be noticed. However, if the electrode is allowed to touch the thin film of sodium oleate solution that crawls up between the glass and the benzene, then the results are obtained as shown in the tables. Due to this effect we cannot be certain just what we are measuring and cannot arrive at definite conclusions as to the change of interfacial tension, as can be when using the drop weight method.

THE CAPILLARY METHOD WITH HIGH POTENTIALS, USING PURE LIQUIDS AGAINST WATER.

DESCRIPTION OF APPARATUS AND MATERIALS:- The apparatus used in this work was the same capillary apparatus used in the previous discussion. The source of potential, however, was obtained from an electrostatic machine run by an electric motor. In this way a potential of several hundred thousand volts could be obtained provided the leaking of electrons was minimized but in some cases the leakage through the capillary apparatus was considerable thus decreasing the potential to possibly 25,000 volts.

The liquids used against water in the system were benzene, nitrobenzene, amylacetate, amyl alcohol, ethyl bromide, carbon disulfide and carbon tetri chloride. Benzene was also used against sodium oleate solution.

METHOD OF PROCEDURE:- The method was the same as that in the previous part. The meniscus of the two liquids was adjusted to the center of the capillary and the change of meniscus noted and the change of interfacial tension was calculated in dynes per centimeter.

In this case, however, it was not necessary to bring the platinum electrode in the second liquid near the interface when a potential was applied.

Table. IV

Water against. liquids.	Water + 2nd liq −	No Potential	Water − 2nd. liq +	No Potential	Water + 2nd. liq. −	No Potential	Water − 2nd liq +	No Potential
Sodium Oleate Solution. Benzene.	−66.	−4.	−66.	−2.	−66.	+2.	−66.	+6
Benzene.	−66.	−5.	−55.	−5	−66.	−5.	−55.	−5.
Nitrobenzene.	−10.	−10.	−10.	−10.	−10.	−10.	−10.	−10.
Amylacetate.	−23.	−3.	+20.	+3.	−23.	−3.	+20.	+3.
Amylalcohal.	−10.	−3.	−10	−3.	−10.	−3.	−10.	−3.
Ethyl Bromide.	+52.	+15.	−225.	−25.	+52.	+10.	−225.	−25.
Carbon disulfide.	0.	0.	0.	0.	0.	0.	0.	0.
Carbon tetrachloride	0.	0.	0.	0.	0.	0.	0.	0.

Using only one Electrode.

Water against.	No Potential	Water + 2nd liq. 0	No Potential	Water. − 2nd. liq. 0	No Potential	Water. 0 2nd. liq. −	No Potential.	Water. 0 2nd liq. +
Benzene.	0.	0.	0.	0.	0.	−5.	−5.	−5.
Ethyl Bromide.	0.	+1.	+1.	+7.	+7.	+1.	+1.	+7.
Amylacetate.	0.	−7.	−3.	+1.	−1.	0.	0.	0.

The normal Interfacial Tensions were not calculated but set equal to zero and the change of Interfacial Tension recorded in dynes per centimeter. The positive and Negative signs before the Numbers indicate an increase and decrease of Interfacial Tension resp.

DISCUSSION:- This effect does not seem to be a change of interfacial tension but more of the nature of attraction and repulsion between unlike and like charged bodies and depending partly on the dielectric constant and the specific nature of the second liquid saturated with water. In all cases the meniscus was concave to the water side although it sometimes tended to flatten out when a high potential was imposed upon it. It was calculated that the change of interfacial tension using benzene as the second liquid was about 65 dynes/cm., less than normal and the normal interfacial tension is only 34.5 dynes/cm. The figures shown in the tables show relatively how different liquids are affected by high potentials. This same effect will be observed by merely touching the platinum electrodes to the glass of the two ends of the capillary apparatus though not so good. In the case of benzene and water, water seems to collect in the benzene on the sides of the large tube. Also violent agitation takes place on the surface of the benzene but not so on the water surface.

THE DROP WEIGHT METHOD USING 300 VOLTS.

DESCRIPTION OF APPARATUS AND MATERIALS:- The apparatus consisted of a pipette with a ground glass tip with a diameter of 4.514 milimeters. The tip was a thick walled glass capillary with a ground flat surface, the outside being polished. The pipette had a volume of 5.22 c.c., between the graduations on either side of the enlargement. Near the top of the pipette, a platinum wire was sealed through the glass and brought down to within an inch and a half of the tip. A second electrode in the form of a ring with a diameter of 1.05 cm., was placed around the forming drop at the point where the drop broke off. A stopcock at the top of the pipette allowed air to enter the pipette slowly from a long drawn out glass capillary. The resistance of the capillary to the passage of air was so great that it allowed a drop of water to fall in benzene about every four minutes. A calcium chloride tube was placed in series with the capillary so the air was thoroughly dried before passing through the capillary so that no moisture could collect inside the capillary and obstruct the passage of air. In order to adjust the level of the liquid in the pipette, a suction tube was connected between the pipette and the capillary. This could be shut off by means of a stopcock. A large flask was placed in series with this suction tube to act as a sort of air cushion when suction was applied.

The source of potential consisted of a small motor generator which produced about one half an ampere at 500 volts direct current. A switch was arranged so that the current could be easily reversed.

Varying concentrations of sodium oleate solution was used against benzene. Pure water was also used against benzene.

METHOD OF PROCEDURE:- The water or sodium oleate solution was drawn up into the pipette and then put in series with the capillary for letting in air. The tip of the pipette was placed about one half a cm., below the surface of a beaker of benzene. It was then made sure that the sodium oleate solution covered all of the ground surface of the pipette tip but did not crawl up the polished side of the capillary. The level of the liquid in the pipette was adjusted by means of the suction tube. The drops were allowed to form slowly and break off. The length of time for each drop to form and break off was found with a stop watch.

In order to prove that the change of interfacial tension under the influence of a potential was due to the presence of the sodium oleate in the interface runs were made using pure water and benzene. The following runs were made and the data graphed:-

The two liquids unsaturated with each other.

1. odd drops -zero potential

   even drops - water −, benzene +

2. odd drops -zero potential

   even drops - water +, benzene −

The two liquids mutually saturated with each other.

3. odd drops -zero potential

even drops -$\frac{\text{water}}{\text{benzene}}$ $\frac{+}{-}$

4. odd drops -zero potential

even drops -$\frac{\text{water}}{\text{benzene}}$ $\frac{-}{+}$

0.1% sodium oleate against benzene mutually saturated with each other.

5. odd drops -zero potential

even drops -$\frac{\text{0.1\% sodium oleate solution}}{\text{benzene}}$ $\frac{+}{-}$

6. odd drops -zero potential

even drops -$\frac{\text{0.1\% sodium oleate solution}}{\text{benzene}}$ $\frac{-}{+}$

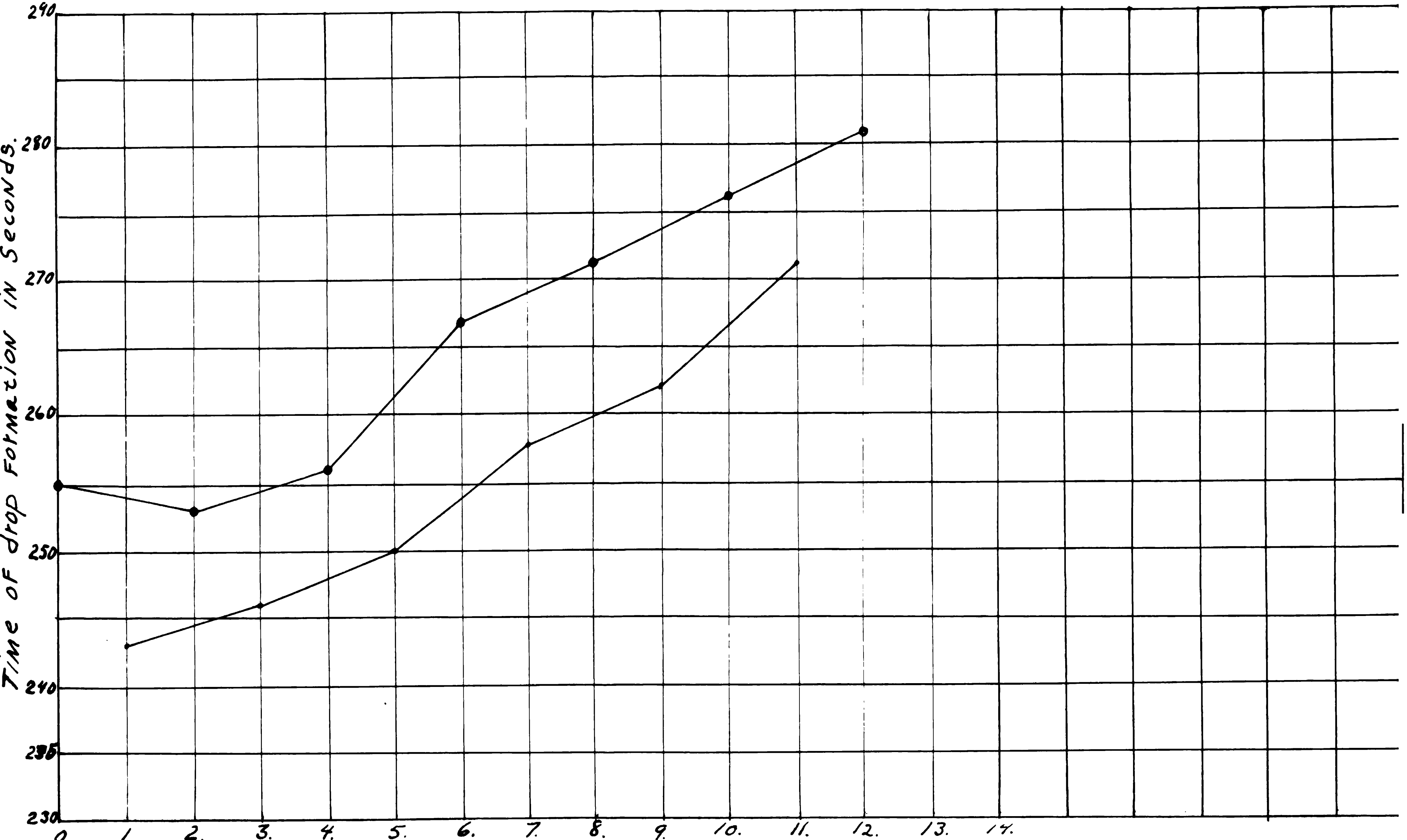
7. odd drops -zero potential

even drops -$\frac{\text{0.01\% sodium oleate solution}}{\text{benzene}}$ $\frac{-}{+}$

TABLE V.

Water against benzene -unsaturated.

Volts	Polarity of water	Polarity of benzene	Time of drop formation in sec.
0	0	0	255.0
300	-	+	245.0
0	0	0	253.0
300	-	+	246.0
0	0	0	256.0
300	-	+	250.0
0	0	0	267.0
300	-	+	253.0
0	0	0	271.0
300	-	+	262.0
0	0	0	276.0
300	-	+	271.0
0	0	0	281.0

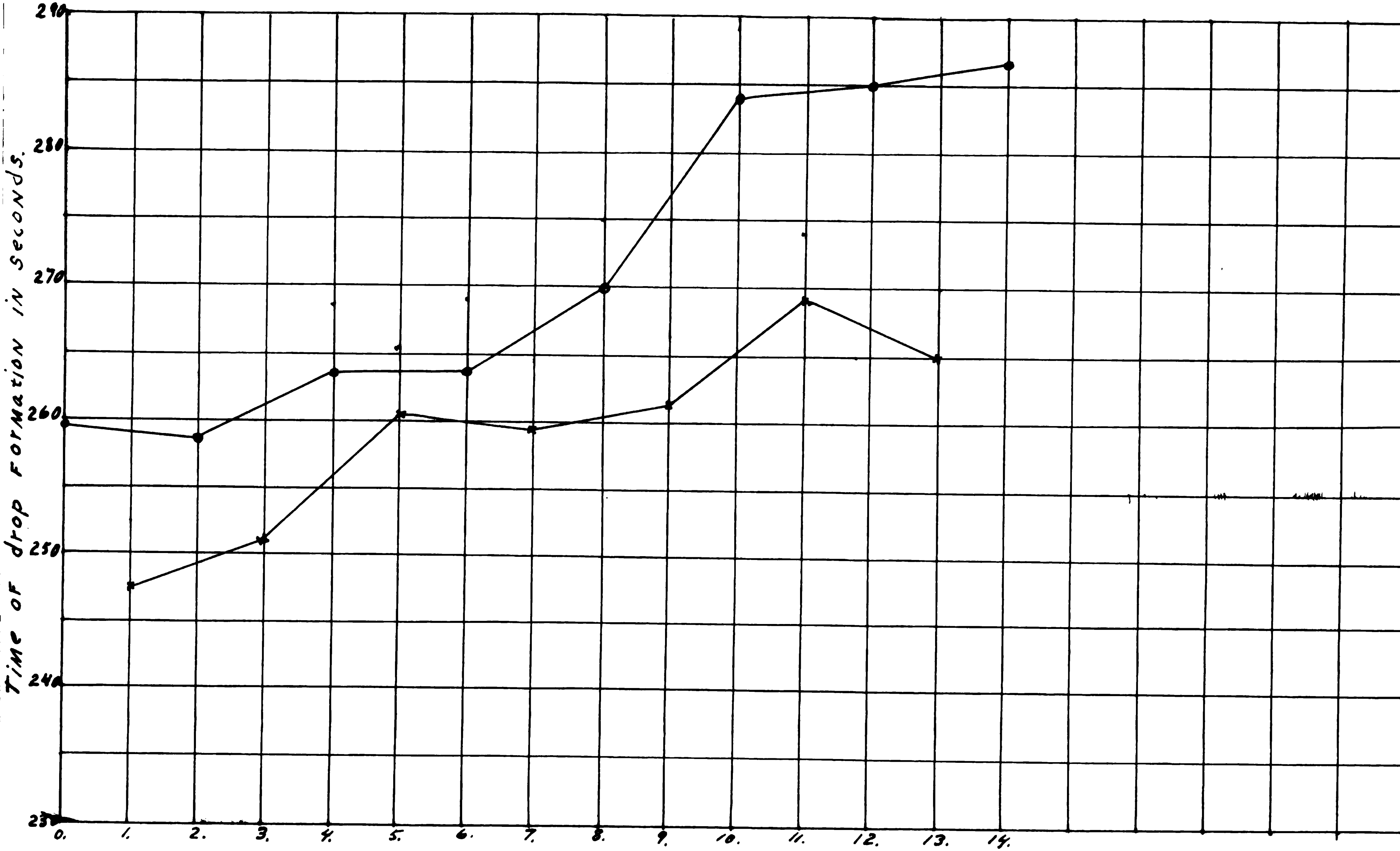


Water unsaturated with benzene against benzene saturated with Water.
• = zero potential; • " Water negative, benzene positive.
Fig. 5.

TABLE VI

Water against benzene -unsaturated.

Volts	Polarity of water	Polarity of benzene	Time of drop formation in sec.
0	0	0	264.5
300	+	-	252.5
0	0	0	269.5
300	+	-	256.0
0	0	0	268.5
300	+	-	265.5
0	0	0	269.0
300	+	-	264.5
0	0	0	275.0
300	+	-	266.5
0	0	0	289.0
300	+	-	274.0
0	0	0	290.0
300	+	-	270.0
0	0	0	292.5

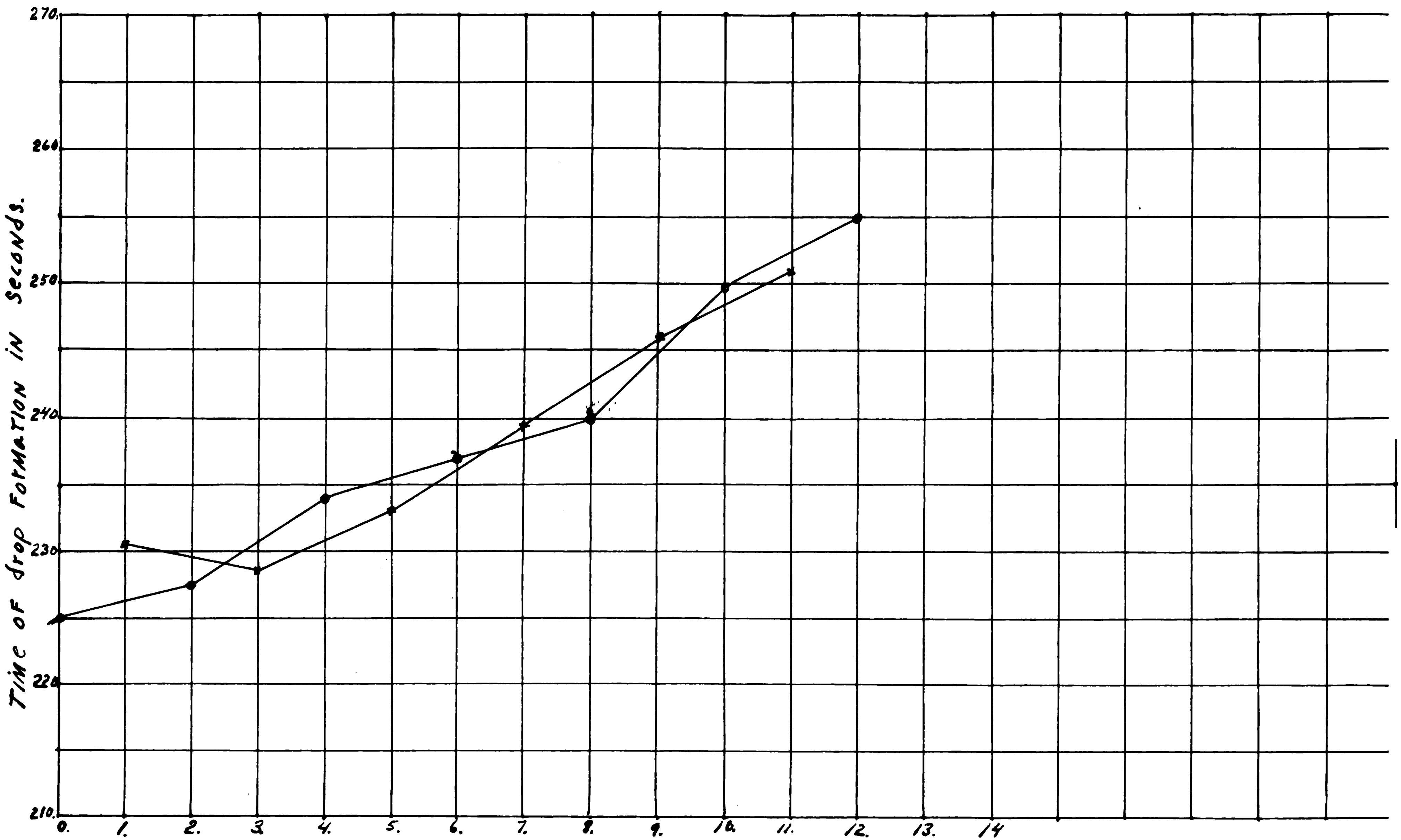


Water unsaturated with benzene against benzene saturated with water.
o = Zero potential ; x = Water positive, benzene negative.
Fig. 6.

TABLE VII.

Water against benzene -saturated.

Volts	Polarity of water	Polarity of benzene	Time of drop formation in sec.	
0	0	0	225.5	
300	+	-		230.5
0	0	0	227.5	
300	+	-		228.5
0	0	0	234.0	
300	+	-		233.0
0	0	0	237.0	
300	+	-		239.5
0	0	0	240.5	
300	+	-		246.0
0	0	0	250.0	
300	+	-		251.0
0	0	0	255.0	

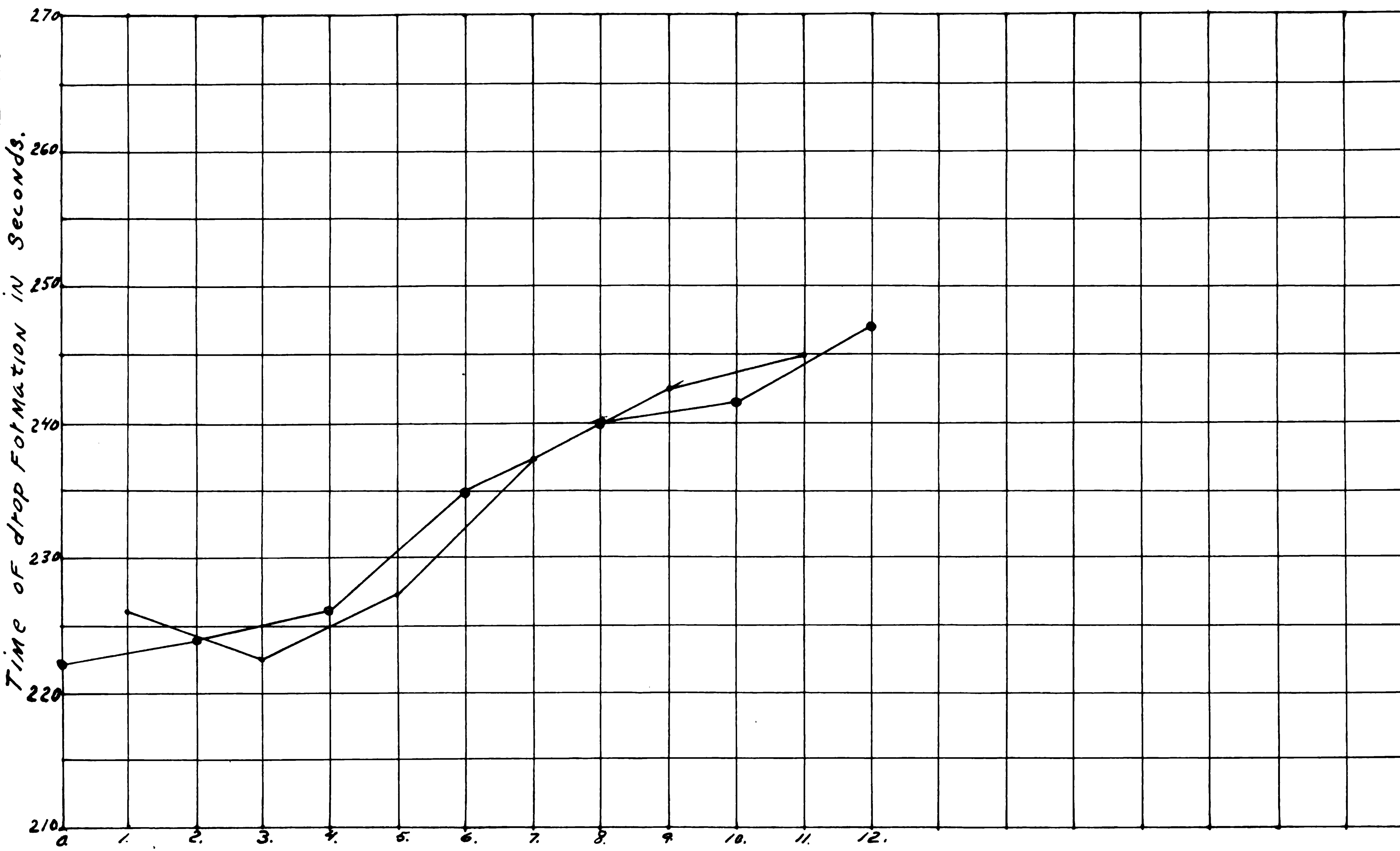


Water saturated with benzene against benzene saturated with water.
o = zero potential ; x = water positive, benzene negative.
Fig. 7.

TABLE VIII

Water against benzene -saturated.

Volts	Polarity of water.	Polarity of benzene.	Time of drop formation in sec.	
0	0	0	222.0	
300	-	+		226.0
0	0	0	224.0	
300	-	+		222.5
0	0	0	226.0	
300	-	+		227.5
0	0	0	235.0	
300	-	+		237.5
0	0	0	240.0	
300	-	+		241.5
0	0	0	245.0	
300	-			247.0

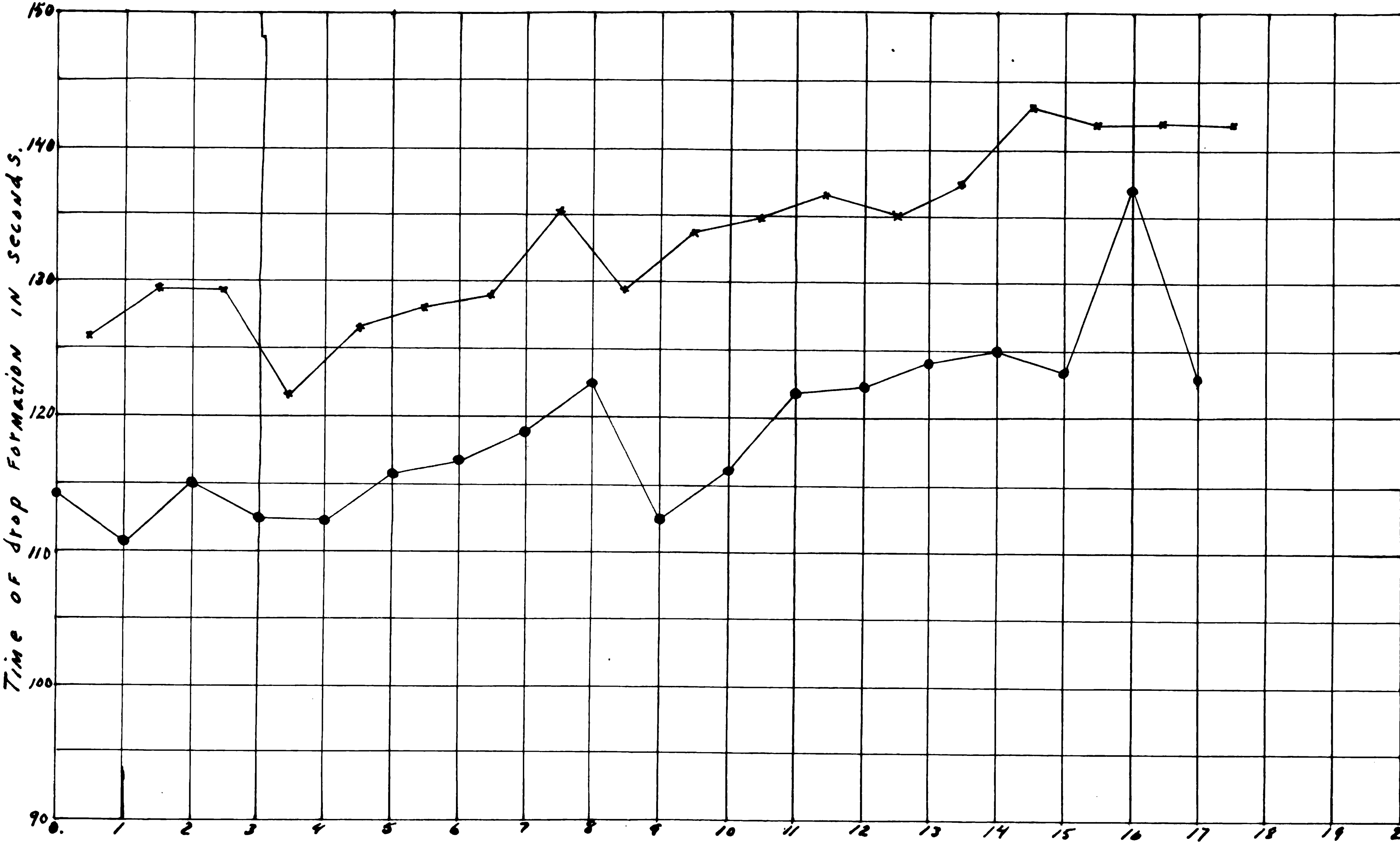


Water saturated with benzene against benzene saturated with water.
o = zero potential ; • = water negative, benzene positive.
Fig. 8.

TABLE IX

0.1% sodium oleate solution against benzene -saturated.

Volts	Polarity of sodium oleate solution	Polarity of benzene	Time of drop formation in sec.
0	0	0	114.0
300	+	-	126.0
0	0	0	110.5
300	+	-	129.5
0	0	0	115.0
300	+	-	129.5
0	0	0	112.5
300	+	-	121.5
0	0	0	112.5
300	+	-	126.5
0	0	0	116.0
300	+	-	123.0
0	0	0	116.5
300	+	-	129.0
0	0	0	119.0
300	+	-	135.0
0	0	0	122.0
300	+	-	129.5
0	0	0	112.5
300	+	-	133.5
0	0	0	116.0
300	+	-	135.0
0	0	0	122.0
300	+	-	136.5
0	0	0	122.0
300	+	-	135.0

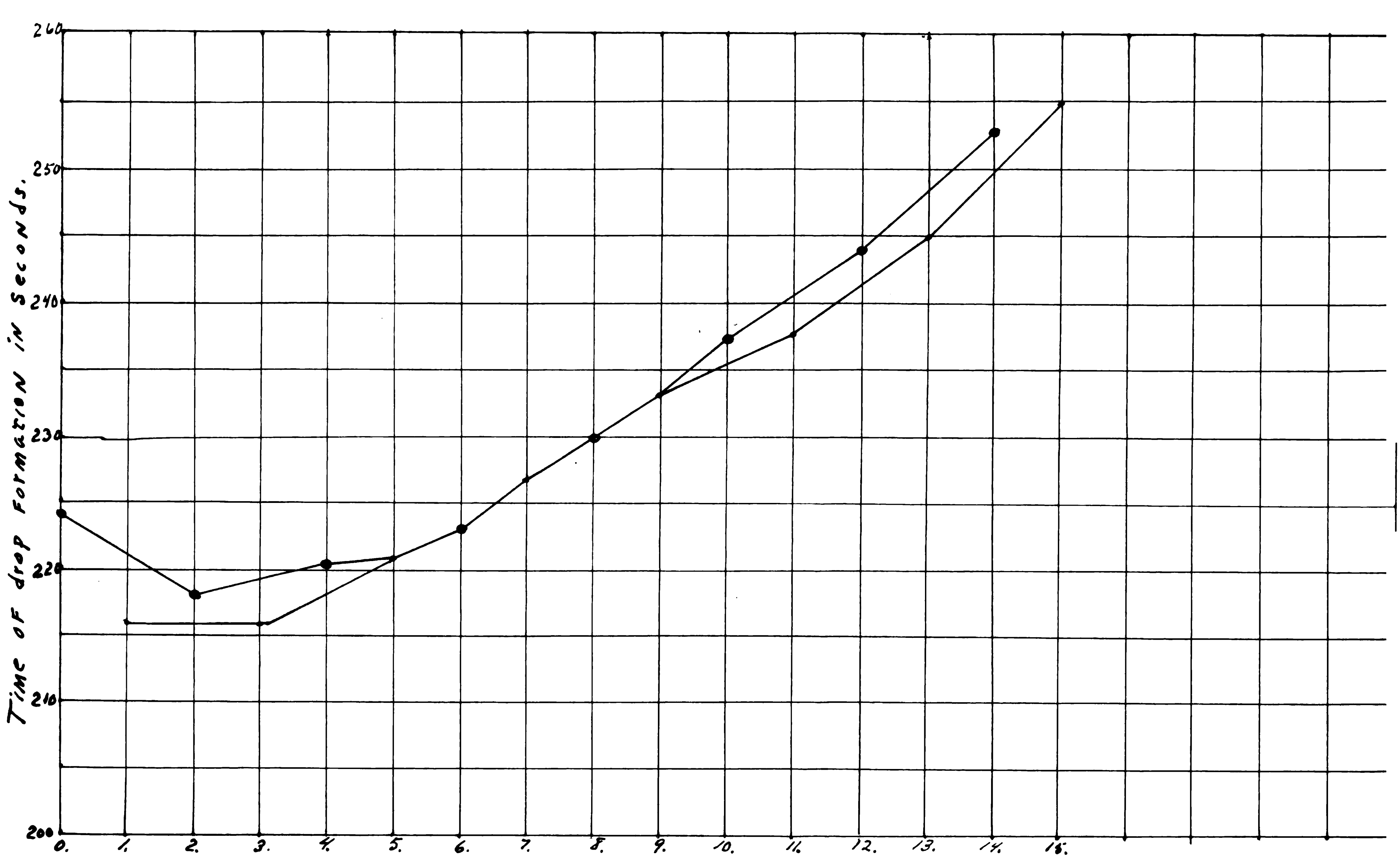


0.1% $C_{17}H_{33}COONa$ Sol'n saturated with benzene against benzene saturated with $C_{17}H_{33}COONa$ sol'n.
o = zero potential; x = Sodium oleate solution positive, benzene negative.
Fig. 9.

TABLE X.

0.1% sodium oleate solution against benzene -saturated.

Volts	Polarity of sodium oleate solution.	Polarity of benzene.	Time of drop formation in sec.
0	0	0	224.0
300	-	+	216.0
0	0	0	218.0
300	-	+	216.0
0	0	0	220.5
300	-	+	221.0
0	0	0	223.0
300	-	+	227.0
0	0	0	230.0
300	-	+	233.0
0	0	0	237.5
300	-	+	237.0
0	0	0	244.0
300	-	+	245.0
0	0	0	253.0
300	-	+	260.0



0.1% $C_{17}H_{33}COONa$ sol'n. saturated with benzene against benzene saturated with $C_{17}H_{33}COONa$ sol'n

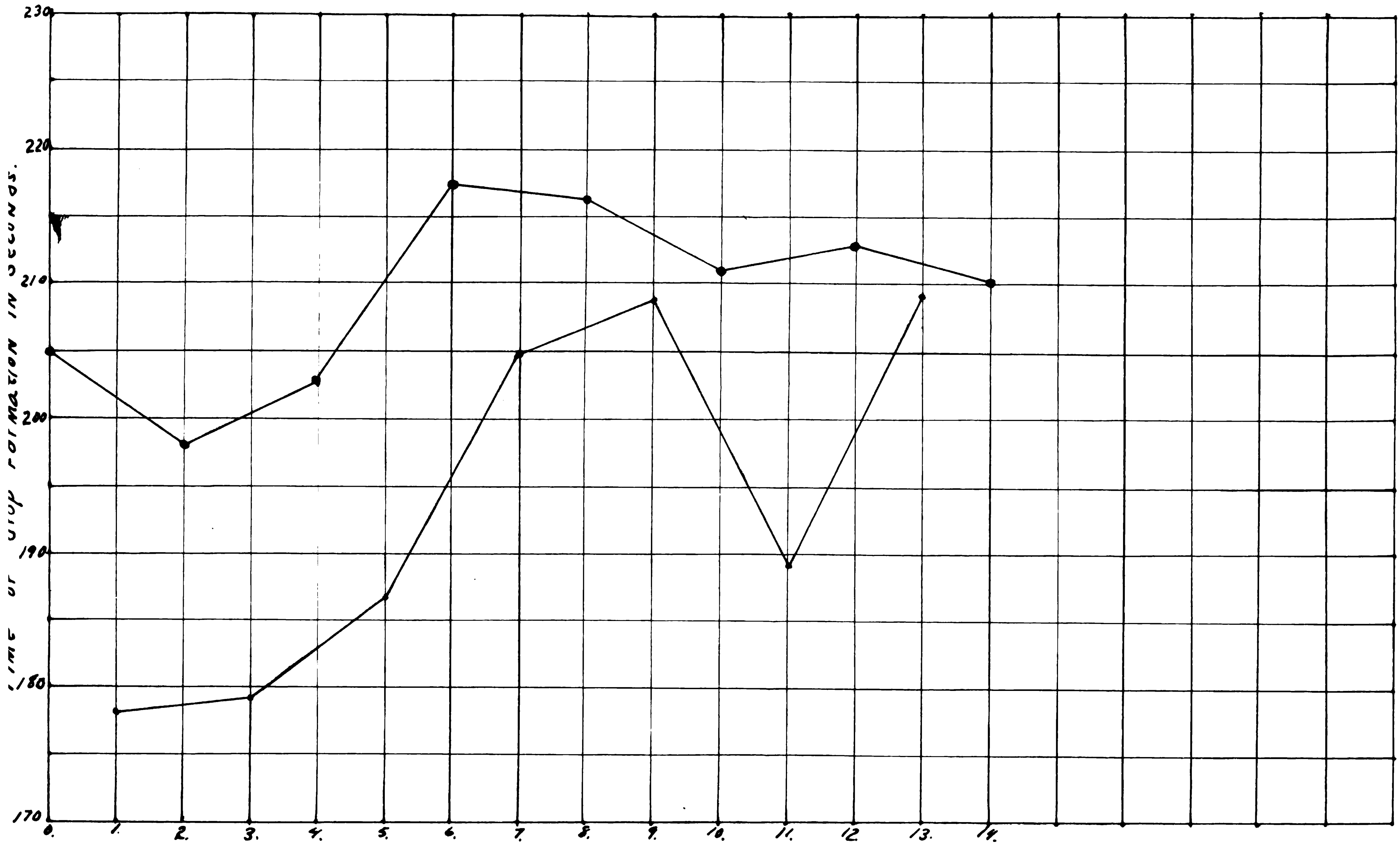
o = zero potential ; · = Sodium Oleate solution negative, benzene positive.

Fig. 10.

TABLE XI.

0.01% sodium oleate solution against benzene -saturated.

Volts.	Polarity of sodium oleate solution.	Polarity of benzene.	Time of drop formation in sec.	
0	0	0	204.5	
300	-	+		178.0
0	0	0	198.0	
300	-	+		179.0
0	0	0	202.5	
300	-	+		185.5
0	0	0	217.0	
300	-	+		204.5
0	0	0	216.0	
300	-	+		208.5
0	0	0	211.0	
300	-	+		189.0
0	0	0	213.0	
300	-	+		209.0
0	0	0	210.0	



0.01 % Sodium oleate solution saturated with benzene against benzene saturated with $C_{17}H_{33}COONa$ Sol'n.
o = zero potential; • = Sodium oleate solution negative, benzene positive.
Fig. 11.

DISCUSSION:- According to Antonow's rule, the interfacial tension between two liquids is equal to the difference of the surface tensions of the two liquids mutually saturated with each other. However, before these unsaturated liquids in contact with each other become saturated there must be a different interfacial tension. It is shown by the first two graphs (Fig. 5&6) how the potential no matter which direction it is directed speeds up the saturation of the water by the benzene,(the benzene was already saturated with water) and thus lowers the interfacial tension which decreases the size of the drop,and this in turn decreases the length of time for the drop to form.

The next two curves (Fig. 7 & 8) are exactly the same system except that the two liquids are mutually saturated with each other. These curves practically coincide with each other which shows that the potential has no influence on the interfacial tensions of mutually saturated liquids.

The next two curves (Fig. 9& 10) are systems of 0.1% sodium oleate solution against benzene mutually saturated with each other. In the case of the polarity of the sodium oleate solution being positive and the benzene negative, there is a decided difference in the length of time for the drops to form (averaging about 15 seconds). We would expect if we consider the sodium as the positive end of the soap mollecule that with this direction of potential there would be a tendancy for the soap mollecules to reorient themselves at 180 to their normal orientation in the interface or else there would be a tendency to decrease the concentration of the soap in the interface and thus increase the interfacial tension and thus increase the length of time for a drop to form and this is exactly what happens. In the case of 0.1% sodium oleate the interfacial tension in about 11.2 dynes per cm. Thus if the volume of the drop is increased about (135/120) the interfacial tension is increased about 1 1/2 dynes/cm.

Using this same system with the potential reversed the two lines of the graph practically coincide, the zero potential line probably being a trifle higher. With the potential in this direction more soap mollecules should be concentrated in the interface and thus the interfacial tension lowered and also the time of drop formation lowered. However, the concentration of soap in the interface is very high at 0.1% sodium oleate solution and the few more that could be crowded into the interface would not hve a very great effect. In order to overcome this a 0.01% sodium oleate solution was used and the last graph was obtained, (Fig 11.). In this graph, although very irregular, there is a decided lowering of the interfacial tension by the potential. As the concentration of the soap in the interface is very small at 0.01% the influence of the potential in concentrating more soap mollecules in the interface is quite great. If the original interfacial tension of 0.01% sodium oleate is 32.2 dynes/cm., and the volume of the drop is decreased about (195/210) of its normal size, then the interfacial tension has changed about 2.3 dynes/cm.

CONCLUSIONS:-

1. The speed of saturation of unsaturated solutions in contact with each other is hastened by the use of a potential.

2. The interfacial tension between two mutually saturated liquids can not be changed by the use of a potential.

3. The concentration of sodium oleate in the interface may be altered or the direction of orientation changed with the influence of a potential. In other words, the interfacial tension may be either increased or decreased in this manner.

4. The sodium oleate mollecule in the interface behaves as though the sodium end were the positive end and the long hydrocarbon chain the negative end.

This work was performed in the Kedzie Chemical Laboratory at Michigan State College under the direction of Dr. Dwight Larbell Ewing.