INTERFACIAL TENSION BY THE RING METHOD IN NON-EQUILIBRIUM LIQUID-LIQUID SYSTEMS

by

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INTRODUCTION

In liquid-liquid extraction, studies have been frequently correlated by means of a capacity coefficient. This coefficient is a product of two terms, an area term and a diffusion rate term. So far little work has been done in devising a means to separate these two terms. For liquid-liquid extraction in a spray tower, one possibility for attacking the problem would appear to be the estimation of the sizes of drops formed at the distributor. From these drop sizes, the total area over which diffusion takes place could be estimated. The drop sizes probably depend on distributor design, flow rate through the distributor, viscosities, densities, and interfacial tension. One of the most important of these factors is interfacial tension. Since the drops are formed while the solute being extracted is not in equilibrium between the two liquid phases, it appears desirable to know something of the interfacial tension in non-equilibrium liquid-liquid systems.

SUMMARY

It was the purpose of this investigation to study the possibilities of applying the ring method to determine interfacial tension in non-equilibrium liquid-liquid systems.

During this work measurements were taken on the systems benzene-acetic acid-water and methyl isobutyl ketone-acetic acid-water with a Cenco du Nouy interfacial tensiometer. The direct evaluation of interfacial tension for given concentrations of solute in the two phases was impossible because after two phases of known acid concentration are brought into contact, time must elapse before an experimental measurement of interfacial tension can be taken, and during this time diffusion of the solute occurs such that uniform concentrations in the two phases do not exist at the instant of measurement. To circumvent this difficulty, two phases whose acid concentrations were known were brought in contact and a series of interfacial tension measurements were taken while diffusion was taking place. These values were then plotted against the time of the measurements and extrapolated to the time at which the two phases were brought into contact. Thus a value of interfacial tension at known uniform acid concentrations in the two phases could be estimated.

The summaries of these measurements are presented in Figures 12 and 19. These show lines of constant interfacial

tension plotted on coordinates of acid concentrations in the two phases. Figure 12, the summary for the benzene-acetic acid-water system, was based on 49 series of measurements; and Figure 19, the summary for the methyl isobutyl ketone-acetic acid-water system, was based on 16 series.

THEORY

True surface tension is defined as the force per centimeter on the surface of a liquid in equilibrium with its vapor which opposes the expansion of the liquid's surface area. Surface tension is due to the unbalanced forces of molecular attraction at the surface of the liquid. Interfacial tensions are related to surface tensions in that they are also a measure of molecular attraction, but in this case the attraction is between unlike molecules. These attractive forces may be measured between immiscible liquids, a liquid and a gas, or a liquid and a solid.

Interfacial tension between two immiscible liquids can be measured by various means[5], including the weighing of drops which fall or rise from a glass tip into an immiscible phase, the determination of the shape of a hanging drop in another phase, the pressure required to form a bubble in an immiscible phase, and the pulling of a ring or staple from the interface of the two liquids. The addition of a solute to a liquid-liquid system may exert a profound influence on the interface, and if this solute is not at equilibrium between the two phases, the procedure which one must follow to measure this interfacial tension must be modified.

Because of the importance of interfacial tension in liquid-liquid extraction, some attempts have been made to

determine interfacial tension in two phase systems in which a solute is not in equilibrium between the two immiscible phases. The only reported experimental measurements of interfacial tensions during non-equilibrium conditions are those published by Browning and Elgin.[3] The measurements were made using the drop weight method on the isopropyl ether-acetic acid-water system. Since this method demands that the drops be formed slowly, account should be taken of the concentration gradients that are created by diffusion of the solute. In the above mentioned work the author stated that three minutes were required to form the drops, but no mention was made of the concentration changes occurring during this time interval.

In the present work interfacial tension at non-equilibrium conditions was measured by the ring method. The ring method involves the measure of the force required to pull a wire ring from the interface of the liquids. One of the most popular instruments which measures this force is the Cenco du Nouy interfacial tensiometer, and such an instrument was used in this work. This instrument is a sensitive torsion balance by means of which a slowly increasing force may be applied to a platinum ring in contact with the interface. The amount of the force is indicated upon a circular graduated scale which, when calibrated, gives the reading directly in dynes per centimeter. The pull on the ring is obtained by applying a torque to a

fine steel wire, fixed at one end and attached at the other to a movable index. A light lever arm of steel clamped to the center of the torsion wire applies the force to the ring suspended from its outer end.[4]

Harkins and Jourdan[7] and Freud and Freud[6] showed that the apparent interfacial tension as determined by the ring method may differ from the true interfacial tension by as much as 30 per cent. These errors are a function of the apparent interfacial tension, the radius of the wire ring, the radius of the wire which forms the ring and the density difference between the two phases. Zuidema and Waters[8] have published a formula which accounts for these factors, and a plot of this equation appears in Figure 20.

With the exception of two variations, operation of the tensiometer was based upon the recommendations made by the manufacturer.[4] The discussion of these variations together with their basis are presented in the procedure.

The validity of the extrapolations on which this report was based could not be closely checked. In making these extrapolations, curves were plotted showing the variation of the apparent interfacial tension with time from the addition of the lighter phase. As may be seen in Figure 1, the slope of the curve becomes greater as the time approaches zero. One very rough check was obtained by applying tension to the ring before the lighter phase was added; it was found that the tension could not be less

than 6.0 dynes per centimeter. This value was 2.9 dynes less than the extrapolated value, and a closer approach to the extrapolated value by this technique was not possible because the addition of the lighter phase caused a slight disturbance at the interface. To see if the disturbances due to the addition of the lighter phase caused this difference, pure methyl isobutyl ketone was added to water in the same manner. By applying tension to the ring before the ketone was added it was found that the ring broke from the interface at values above 8.2 dynes. The interfacial tension of these two phases after the two phases had settled was 11.0 dynes per centimeter. This difference was also 2.8 dynes. Therefore, it may be assumed that the apparent interfacial tension does not lie far below the extrapolated value. It was assumed that the apparent interfacial tension was not greater than the extrapolated value because the ring always broke loose at points lying below the extrapolated value. In Figure 1 it can also be seen that duplicate runs give values which are within the accuracy of the tensiometer ($\pm$ 0.1 dyne).

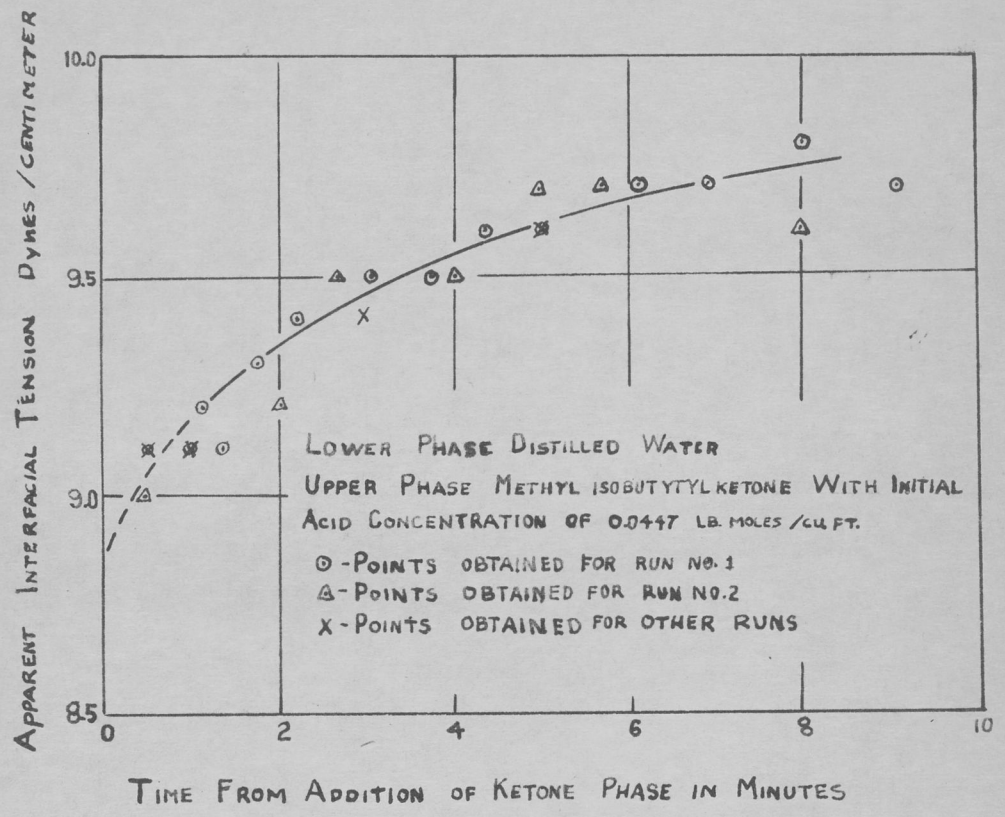

FIG. 1 INTERFACIAL TENSION MEASUREMENTS SHOWING CHECKING POINTS

MATERIALS AND EQUIPMENT

Interfacial tension measurements were made with a Cenco du Nouy interfacial tensiometer NO. 70540 manufactured by the Central Scientific Corporation. A six centimeter platinum ring was used with this instrument.

Liquids used in this experimental work were: C. P. reagent grade glacial acetic acid, thiophene reagent grade benzene, practical grade methyl-isobutyl ketone from Eastman Kodak and Company, Rochester, New York, laboratory distilled water, standard sodium hydroxide solutions, and an alcohol solution of phenolphthalein.

PROCEDURE

In making surface and interfacial tension measurements, one of the most important considerations is that of cleanliness of the articles which come in contact with the liquids on whose surface the measurements are made. Throughout this work this point was kept in mind. Glassware was cleaned with a saturated solution of potassium dichromate in sulfuric acid. After this treatment the articles were thoroughly rinsed with distilled water and allowed to dry. The tensiometer ring was cleaned in the same way but in addition it was heated to a white heat in a reducing flame.

Seven different mixtures of benzene and water containing different quantities of acetic acid were shaken vigorously, and each was allowed to separate into two immiscible phases. Each of these phases was drawn off and portions were titrated with standard sodium hydroxide solution using phenolphthalein as the indicator. Specific gravities were then determined by a chain type Westphal balance.

Before making interfacial tension measurements, the standard procedure for calibration of the tensiometer was carried out. This involved placing 500 to 800 milligrams of weights on the platinum ring and adjusting the lever arms of the instrument so that the dial would read directly in dynes per centimeter. At frequent intervals this

calibration was checked to insure correct readings.

During ordinary interfacial measurements, the heavier phase is placed in a container and is then brought to a position so that the platinum ring lies about five millimeters below the surface of the liquid. The lighter phase is then poured onto the surface of the heavier phase. The depth of the light phase must be great enough to prevent the ring from entering the upper surface prior to breaking from the interface. Torque is gradually applied to the lever arm of the tensiometer while the container is lowered to maintain a horizontal position for the lever arm. When the ring breaks from the interface the dial reading gives directly the apparent interfacial tension. The recommended procedure is to take only one measurement before the ring is cleaned.

Since the basis of this report lies in the extrapolation of a series of interfacial tension measurements to the time at which the lighter phase was added, it was desired to have a method for adding the lighter phase in such a manner that the disturbance at the interface was a minimum. Also it was desired to be able to start a series of measurements at a given time. Thus a 10 milliliter pipette was filled, and as quickly as possible a gummed label was placed over the suction end. This allowed the fastening of the pipette to a ring stand in such a manner that delivery would be directed to the sides of a 50

milliliter beaker which contained 10 milliliters of the water phase. When a run was to commence, the gummed label was removed and measurements were started. The first readings were taken ranging from five to thirty seconds after the start of the addition of the upper phase. These times depended somewhat upon properties of the solutions but mostly upon the dexterity of the operator. Measurements were continued for approximately three minutes to yield the points for one extrapolation. As could be seen in Figure 1, a series of such measurements could be duplicated within the accuracy of the tensiometer.

Interfacial tension measurements were taken between all of the possible starting concentration combinations of the two phases for each system covered in this report. Thus for seven concentrations of acetic acid in each benzene and water solution, 49 combinations resulted, all of which were investigated. Only 16 combinations were studied in the methyl isobutyl ketone-acetic acid-water system.

Temperature variation during all measurements was not more than two degrees from 83 degrees Fahrenheit.

RESULTS

The data presented in this report are divided into two groups. One covers the benzene-acetic acid-water system; the other the methyl isobutyl ketone-acetic acid-water system.

Table I shows equilibrium distribution and specific gravities for the benzene-acetic acid-water system. Table II gives the variation of apparent interfacial tension with time for all the combinations of the solutions shown in Table I. In each of these cases approximately 10 milliliters of each phase was used, and the contact area was about 1.92 square inches. Figures 2 through 9 show the points of Table II in graphical form. These curves were used in the extrapolations previously discussed. The results of the extrapolations are presented in Table III. Table IV gives the correction factors for the values in Table III which, when multiplied by the apparent interfacial tensions in Table III, give the true interfacial tensions in Table V. Table V is represented in Figures 10 and 11 in graphical form. From these figures the final summary of the benzene-acetic acid-water system was constructed. This appears in Figure 12 in which lines of constant interfacial tension are plotted on coordinates of acid concentrations in the two phases.

A similar series of tables and figures is repeated

for the methyl isobutyl ketone-acetic acid-water system. Table VI shows equilibrium data and specific gravities of the solutions in the system. Table VII gives the variation of apparent interfacial tension with time for all possible combinations of the two phases in Table VI. Again in each case approximately 10 milliliters of each phase was used, and the contact area was 1.92 square inches. Figures 13 through 16 show the points of Table VII in graphical form. These curves as before were extrapolated to produce the apparent interfacial tensions found in Table VIII. Table IX indicates the correction factors for the values in Table VIII. The true interfacial tensions are presented in Table X. These values appear graphically in Figure 17 and 18. From a cross plot of Figures 17 and 18, the summary, Figure 19, was constructed for the methyl isobutyl ketone-acetic acid-water system. Figure 19 shows lines of constant interfacial tension on coordinates of acid concentrations in the two phases.

TABLE I

EQUILIBRIUM DISTRIBUTION AND SPECIFIC GRAVITIES

Benzene - Acetic Acid - Water

83°F ± 2°

Water Phase		Benzene Phase	
Specific Gravity	Acid Concentration lb. mols/cu. ft.	Specific Gravity	Acid Concentration lb. mols/cu.ft.
0.9981	0.00	0.8604	0.00
1.0134	0.1608	0.8686	0.01729
1.0298	0.2967	0.8707	0.0282
1.0380	0.384	0.8731	0.0440
1.0439	0.499	0.8772	0.0747
1.0440	0.635	0.8872	0.1462
1.0212	0.669	0.9104	0.310

TABLE II

EXPERIMENTAL DATA: APPARENT INTERFACIAL TENSION VS TIME

Benzene-Acetic Acid-Water

Legend: c = Initial acid concentration in the benzene phase, lb. moles/cu. ft.
w = Initial acid concentration in the water phase, lb. moles/cu. ft.
t = Time of reading in seconds from the addition of the benzene phase
x = The apparent interfacial tension measurement, dynes/centimeter

c = 0.01729 w = 0.000		c = 0.0282 w = 0.000		c = 0.0440 w = 0.000		c = 0.0747 w = 0.000		c = 0.1462 w = 0.000		c = 0.310 w = 0.000	
t	x	t	x	t	x	t	x	t	x	t	x
10	29.4	15	26.4	20	23.8	15	20.9	15	16.7	15	9.3
30	29.8	40	26.7	50	24.7	40	21.4	40	17.4	40	10.1
50	30.1	65	26.9	75	25.1	60	21.9	55	17.7	55	10.3
80	30.4	90	27.1	85	25.2	75	22.3	75	17.9	75	10.5
115	30.5	120	27.2	105	25.2	105	22.5	90	18.0	100	10.7
140	30.5	150	27.3	130	25.4	125	22.6	105	18.1	125	10.8
165	30.5	180	27.4	155	25.4	150	22.8	120	18.2	150	11.1
				180	25.5	180	23.0	140	18.4	180	11.1
								160	18.5		

c = 0.000 w = 0.1608		c = 0.0282 w = 0.1608		c = 0.0440 w = 0.1608		c = 0.0747 w = 0.1608		c = 0.1462 w = 0.1608		c = 0.310 w = 0.1608	
t	x	t	x	t	x	t	x	t	x	t	x
15	20.3	20	18.0	20	16.8	15	14.8	20	11.8	15	7.4
40	20.1	40	17.9	35	16.9	45	15.2	40	12.6	25	7.8
65	19.9	60	18.2	60	17.1	75	15.4	55	12.6	40	8.3
100	19.9	80	18.2	85	17.2	95	15.4	75	13.1	55	8.6
130	19.6	110	18.2	115	17.3	120	15.7	105	13.4	70	8.9
160	19.8	135	18.2	140	17.2	150	16.0	145	13.6	100	9.3
180	19.8	170	18.2	180	17.3	185	16.0	180	13.7	120	9.4
										160	9.8
										180	9.8

TABLE II (continued)

EXPERIMENTAL DATA: APPARENT INTERFACIAL TENSION VS TIME

Benzene-Acetic Acid-Water

Legend: c = Initial acid concentration in the benzene phase, lb. moles/cu. ft.
w = Initial acid concentration in the water phase, lb. moles/cu. ft.
t = Time of reading in seconds from the addition of the benzene phase
x = The apparent interfacial tension measurement, dynes/centimeter

c = 0.01729 w = 0.1608		c = 0.000 w = 0.2967		c = 0.01729 w = 0.2967		c = 0.0282 w = 0.2967		c = 0.0440 w = 0.2967		c = 0.0747 w = 0.2967	
t	x	t	x	t	x	t	x	t	x	t	x
20	18.7	10	13.9	10	13.1	20	12.7	20	12.1	20	11.0
45	18.9	25	13.5	20	13.2	35	12.8	40	11.9	40	11.2
70	19.0	40	13.6	35	13.1	60	12.9	60	12.1	65	11.3
85	18.8	60	13.4	60	13.2	80	12.8	90	12.0	95	11.4
115	18.7	100	13.3	90	13.1	105	12.7	115	12.0	130	11.5
140	18.7	140	13.4	120	13.2	125	12.8	150	12.0	160	11.5
170	18.7			180	13.1	140	12.9				
						160	12.8				

c = 0.1462 w = 0.2967		c = 0.310 w = 0.2967		c = 0.000 w = 0.384		c = 0.1729 w = 0.384		c = 0.0282 w = 0.384		c = 0.0440 w = 0.384	
t	x	t	x	t	x	t	x	t	x	t	x
20	8.9	15	5.5	10	11.1	15	10.7	20	10.1	15	9.8
40	9.3	35	5.8	25	10.8	35	10.5	40	9.9	35	9.8
60	9.6	60	6.0	45	10.5	60	10.3	60	9.8	60	9.8
95	9.8	80	6.4	65	10.2	90	10.2	90	9.7	85	9.8
120	10.0	105	6.3	90	10.2	120	10.2	120	9.7	110	9.9
160	10.1	140	6.6	120	10.2			150	9.6	140	9.8
		180	6.8	180	10.2					180	9.8

TABLE II (continued)

EXPERIMENTAL DATA: APPARENT INTERFACIAL TENSION VS TIME

Benzene-Acetic Acid-Water

Legend: c = Initial acid concentration in the benzene phase, lb. moles/cu. ft.
w = Initial acid concentration in the water phase, lb. moles/ cu. ft.
t = Time of reading in seconds from the addition of the benzene phase
x = The apparent interfacial tension measurement, dynes/centimeter

c = 0.0747 w = 0.384		c = 0.1462 w = 0.384		c = 0.310 w = 0.384		c = 0.000 w = 0.499		c = 0.01729 w = 0.499		c = 0.0282 w = 0.499	
t	x	t	x	t	x	t	x	t	x	t	x
20	8.9	10	6.9	20	4.7	20	8.5	20	8.2	20	7.9
45	9.0	30	7.1	45	5.0	40	8.3	40	8.0	40	7.7
75	8.9	45	7.2	70	5.1	55	8.2	60	7.8	70	7.6
90	9.0	65	7.2	100	5.2	80	8.0	95	7.6	90	7.5
120	9.1	85	7.3	125	5.2	95	7.8	145	7.5	115	7.4
135	9.0	120	7.4	160	5.3	160	7.6	180	7.5	160	7.3
180	9.1	180	7.5								

c = 0.0440 w = 0.499		c = 0.0747 w = 0.499		c = 0.1462 w = 0.499		c = 0.310 w = 0.499		c = 0.000 w = 0.635		c = 0.01729 w = 0.635	
t	x	t	x	t	x	t	x	t	x	t	x
20	7.1	20	7.0	20	5.5	10	3.2	15	4.3	20	4.1
40	7.1	35	7.1	35	5.7	25	3.6	40	4.0	45	4.1
55	7.0	65	7.0	55	5.7	50	4.0	65	3.8	70	4.0
75	6.9	95	7.0	80	5.8	85	4.2	95	3.7	90	4.1
100	6.8	130	7.1	110	5.9	115	4.3	135	3.6	150	4.1
120	6.9	160	6.9	160	6.0	135	4.5	180	3.5	180	4.0
150	6.8	180	7.0	180	5.8	180	4.5				

TABLE II (continued)

EXPERIMENTAL DATA: APPARENT INTERFACIAL TENSION VS TIME

Benzene-Acetic Acid-Water

Legend: c = Initial acid concentration in the benzene phase, lb. moles/cu. ft.
w = Initial acid concentration in the water phase, lb. moles/cu. ft.
t = Time of reading in seconds from the addition of the benzene phase
x = The apparent interfacial tension measurement, dynes/centimeter

c = 0.0282 w = 0.635		c = 0.0440 w = 0.635		c = 0.0747 w = 0.635		c = 0.1462 w = 0.635		c = 0.310 w = 0.635		c = 0.01729 w = 0.669	
t	x	t	x	t	x	t	x	t	x	t	x
15	4.0	15	3.7	15	3.5	10	3.0	15	1.9	30	1.7
35	3.9	40	3.6	40	3.4	20	3.2	45	2.1	60	1.7
55	3.8	60	3.4	60	3.7	45	3.2	75	2.1	90	1.6
80	3.9	80	3.3	95	3.5	60	3.1	105	2.2	110	1.5
100	4.1	100	3.4	115	3.5	85	3.0	140	2.3	150	1.6
120	4.0	135	3.2	145	3.7	115	3.0	180	2.3	180	1.5
140	4.0	165	3.0	180	3.5	135	3.1				
165	3.5	180	2.9			180	3.1				

c = 0.0282 w = 0.669		c = 0.0440 w = 0.669		c = 0.0747 w = 0.669		c = 0.1462 w = 0.699		c = 0.310 w = 0.669		c = 0.000 w = 0.669	
t	x	t	x	t	xx	t	x	t	x	t	x
20	1.6	15	1.4	10	1.3	10	1.3	20	1.0	20	1.9
35	1.4	45	1.4	30	1.3	30	1.3	60	1.0	45	1.7
45	1.6	75	1.3	45	1.3	45	1.3	120	1.0	80	1.5
70	1.5	120	1.3	75	1.3	100	1.4	130	1.0	125	1.4
130	1.5	180	1.4	120	1.3	120	1.3	160	1.0	160	1.4
150	1.5			150	1.3	180	1.3	180	1.0	180	1.4
180	1.5										

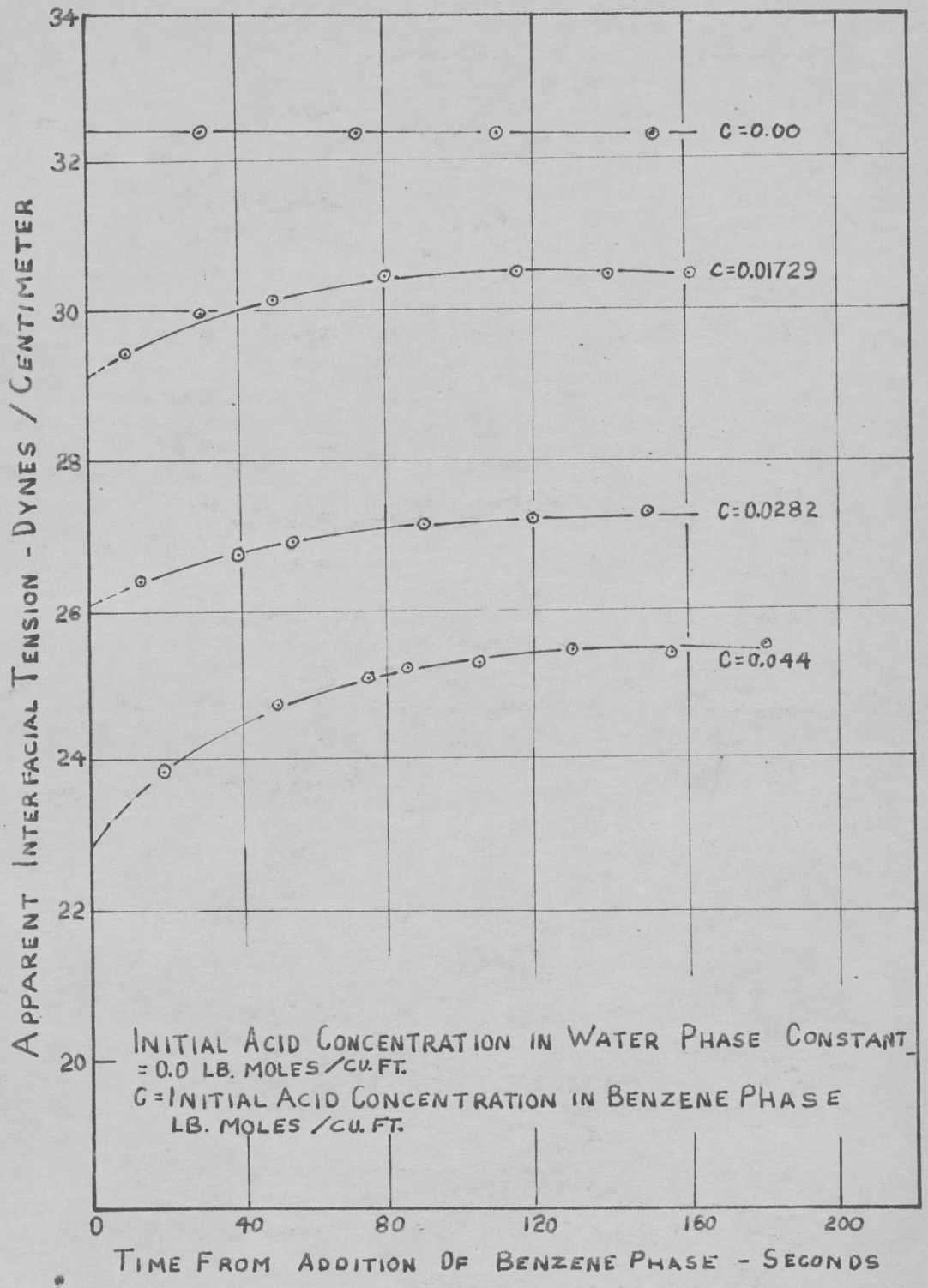

FIG. 2. VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE - ACETIC ACID - WATER 83±2°F.

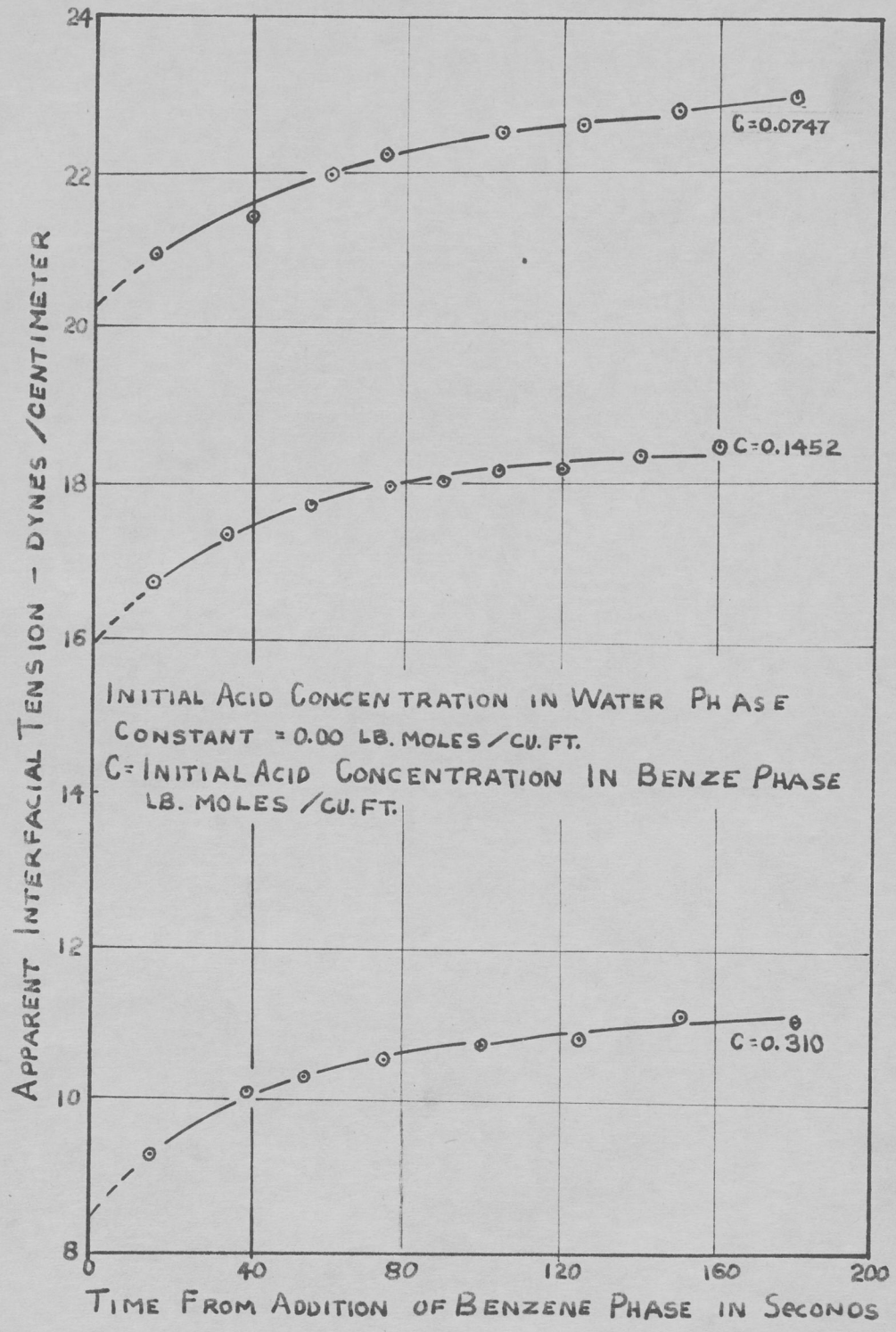

FIG. 3 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME — BENZENE-ACETIC ACID-WATER 83±2°F

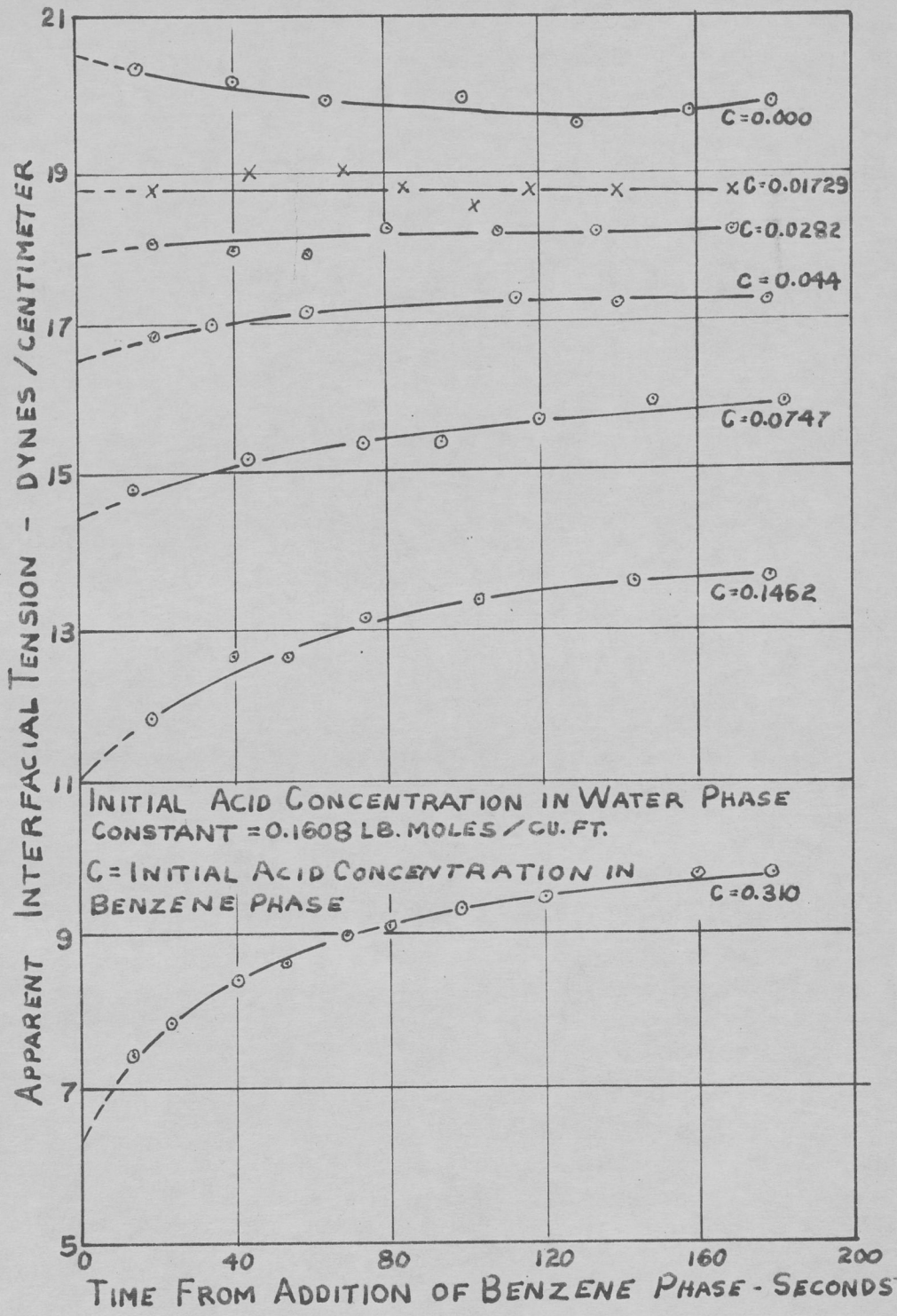

FIG. 4 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE-ACETIC ACID-WATER 83 ± 2°F

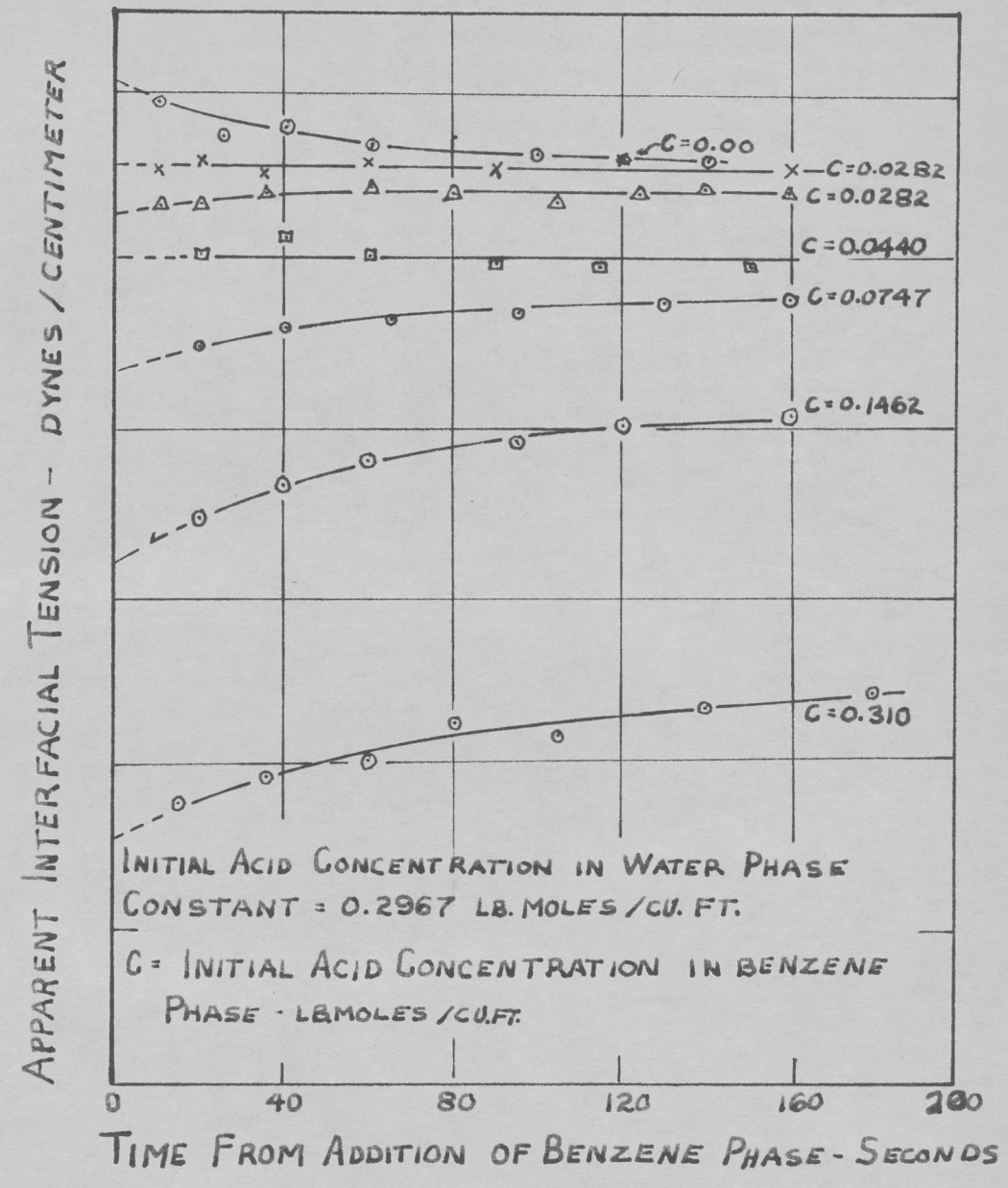

FIG. 5 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE-ACETIC ACID-WATER. 83±2°F

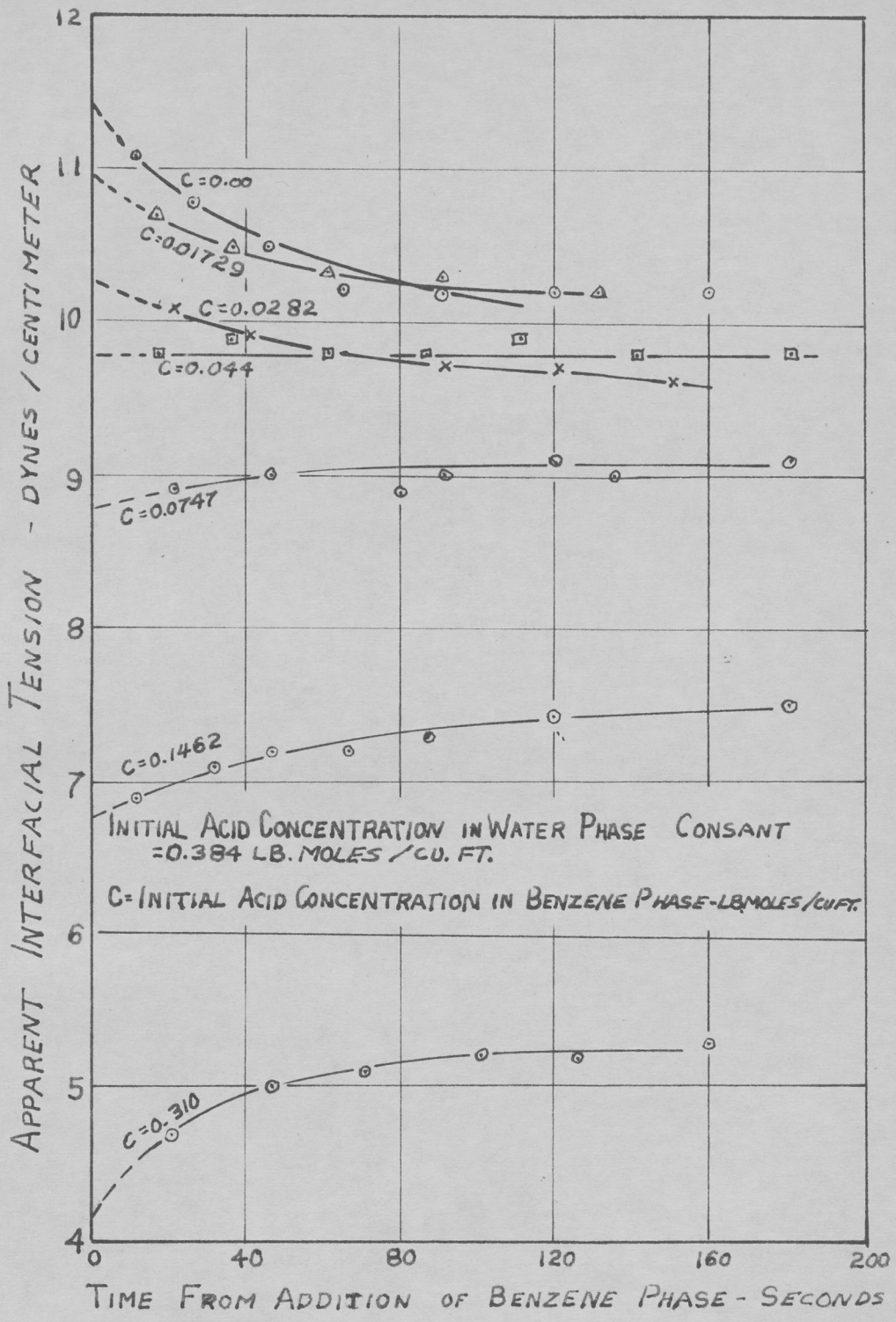

FIG. 6 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE-ACETIC ACID-WATER-83±2°F

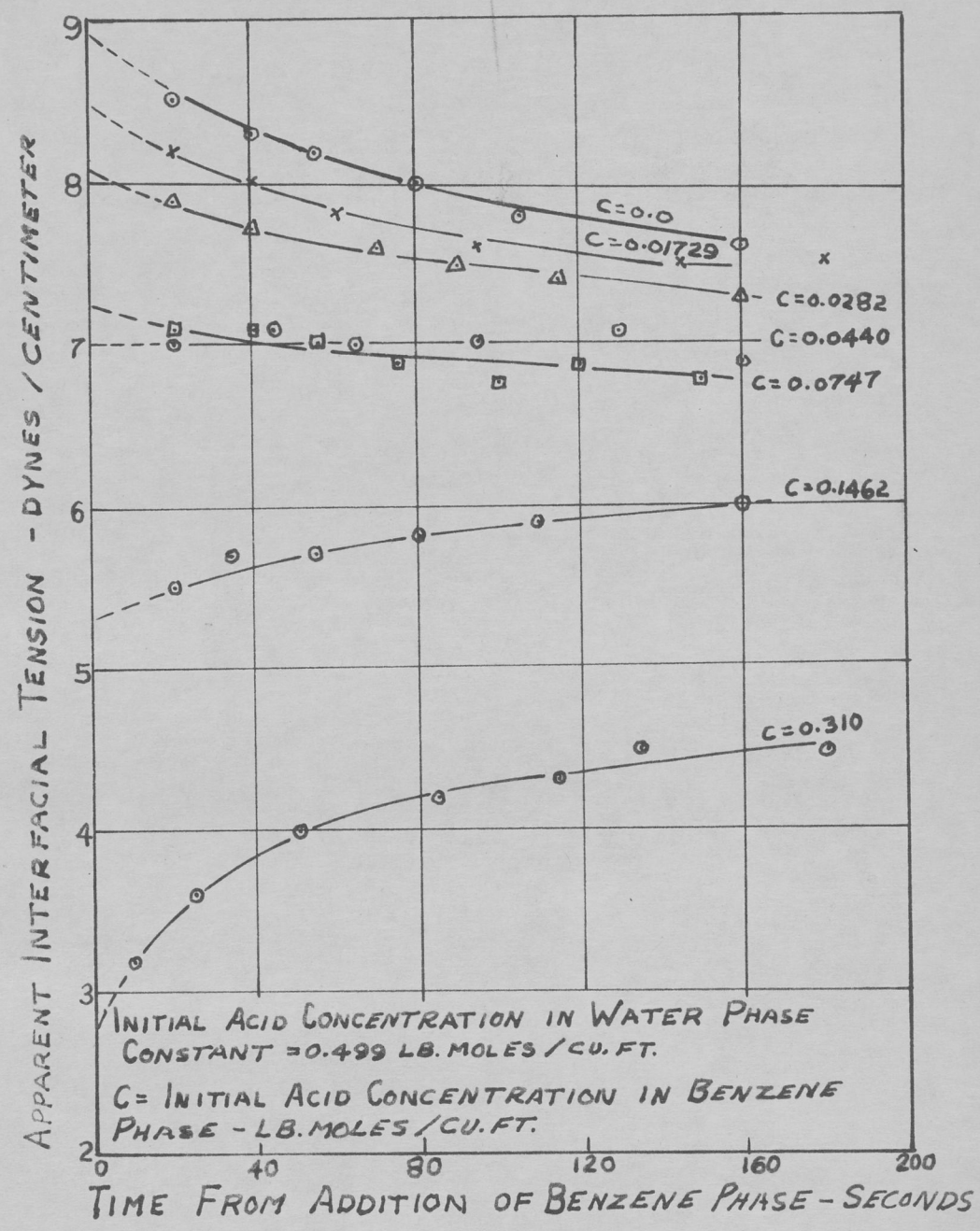

FIG. 7 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE-ACETIC ACID-WATER SYSTEM 83 ± 2 °F

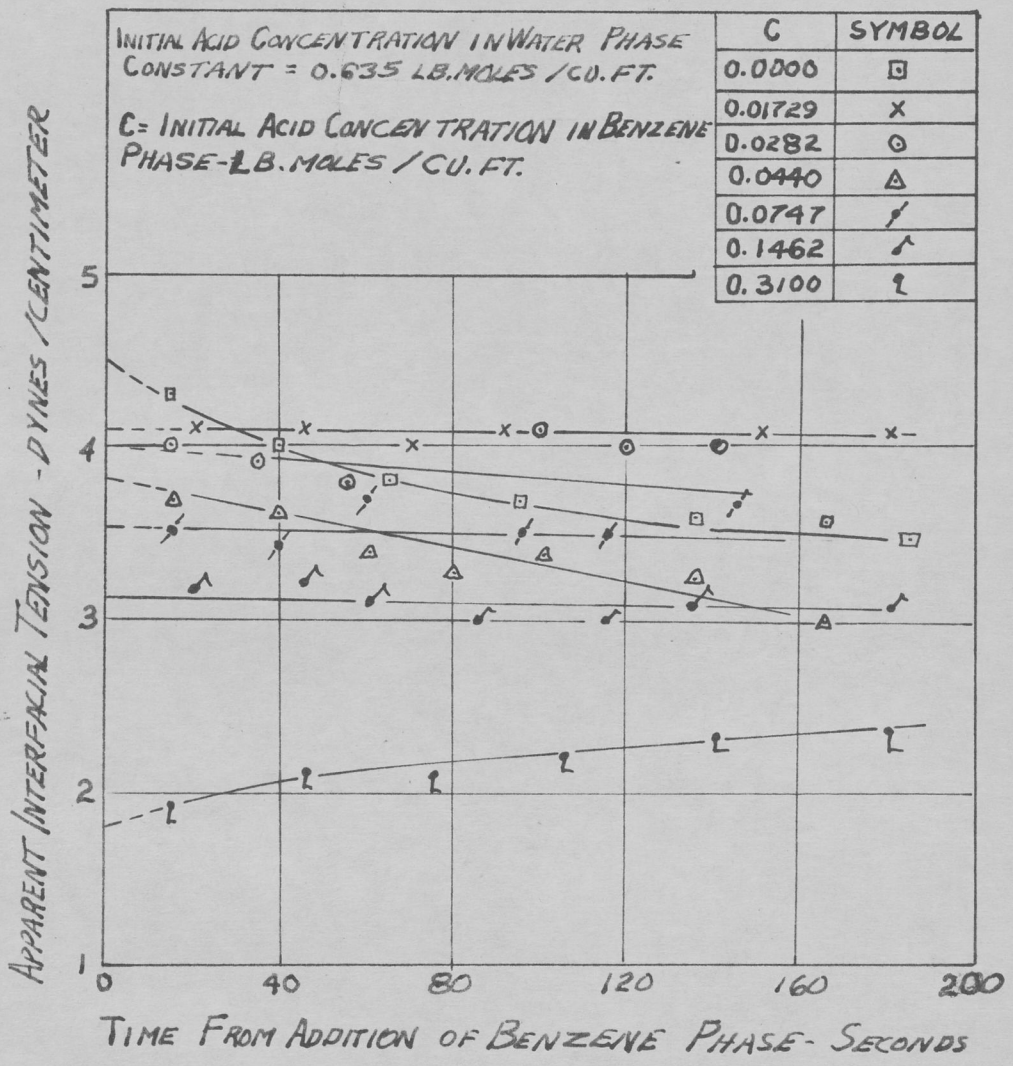

FIG. 8 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE - ACETIC ACID - WATER - 83 ± 2 °F

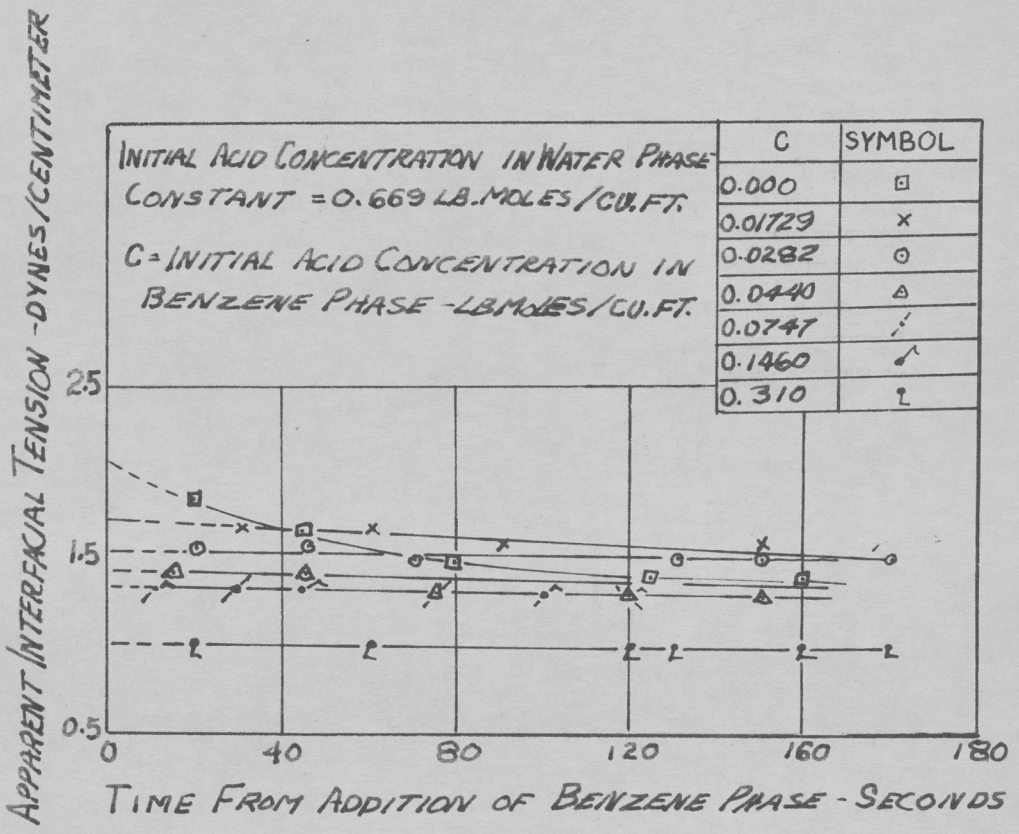

FIG. 9 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME - BENZENE-ACETIC ACID-WATER 83 ± 2°F

TABLE III

APPARENT INTERFACIAL TENSION

Benzene - Acetic Acid - Water

83°F ± 2°

Acid Concentration in the Benzene Phase lb. moles/cu. ft.	Acid Concentration in Water Phase lb. moles/cu. ft.						
	0.00	0.1608	0.2967	0.384	0.499	0.635	0.669
0.00	32.4	20.5	14.1	11.5	8.9	4.5	2.1
0.01729	29.2	18.7	13.0	11.0	8.5	4.1	1.8
0.0282	26.1	17.9	12.6	10.3	8.1	4.0	1.5
0.0440	23.0	16.5	12.0	9.8	7.2	3.8	1.4
0.0747	20.4	14.4	10.7	8.8	7.0	3.5	1.3
0.1462	16.0	11.0	8.4	6.8	5.3	3.1	1.3
0.310	8.6	6.3	5.1	4.2	2.8	1.8	1.0

TABLE IV

CORRECTION FACTORS FOR THE APPARENT INTERFACIAL TENSION

Benzene - Acetic Acid - Water

83°F ± 2°

Acid Concentration in Benzene Phase lb. moles/cu. ft.	Acid Concentration in Water Phase Lb. moles/cu. ft.						
	0.00	0.1608	0.2967	0.384	0.499	0.635	0.669
0.00	1.059	0.984	0.94	0.923	0.906	0.877	0.857
0.01729	1.054	0.981	0.939	0.923	0.905	0.875	0.857
0.0282	1.04	0.978	0.938	0.919	0.904	0.874	0.854
0.0440	1.024	0.971	0.934	0.917	0.900	0.873	0.854
0.0747	1.014	0.960	0.937	0.912	0.899	0.872	0.853
0.1462	0.994	0.944	0.916	0.902	0.889	0.869	0.854
0.310	0.958	0.919	0.900	0.887	0.872	0.860	0.853

TABLE V

TRUE INTERFACIAL TENSION

Benzene - Acetic Acid - Water

83°F ± 2°; dynes/centimeter

Acid Concentration in Benzene Phase lb. moles/cu. ft. \ Acid Concentration in the Water Phase lb. moles/cu. ft.	0.00	0.1608	0.2967	0.384	0.499	0.635	0.669
0.00	34.3	20.2	13.3	10.6	8.1	3.9	1.8
0.01729	30.8	18.4	12.3	10.2	7.7	3.6	1.5
0.0282	27.1	17.5	11.8	9.5	7.3	3.5	1.3
0.0440	23.6	16.0	11.2	9.0	6.5	3.3	1.2
0.0747	20.7	13.8	9.9	8.0	6.3	3.1	1.1
0.1462	15.9	10.4	7.7	6.1	4.7	2.7	1.1
0.310	8.2	5.8	4.6	3.7	2.5	1.6	0.9

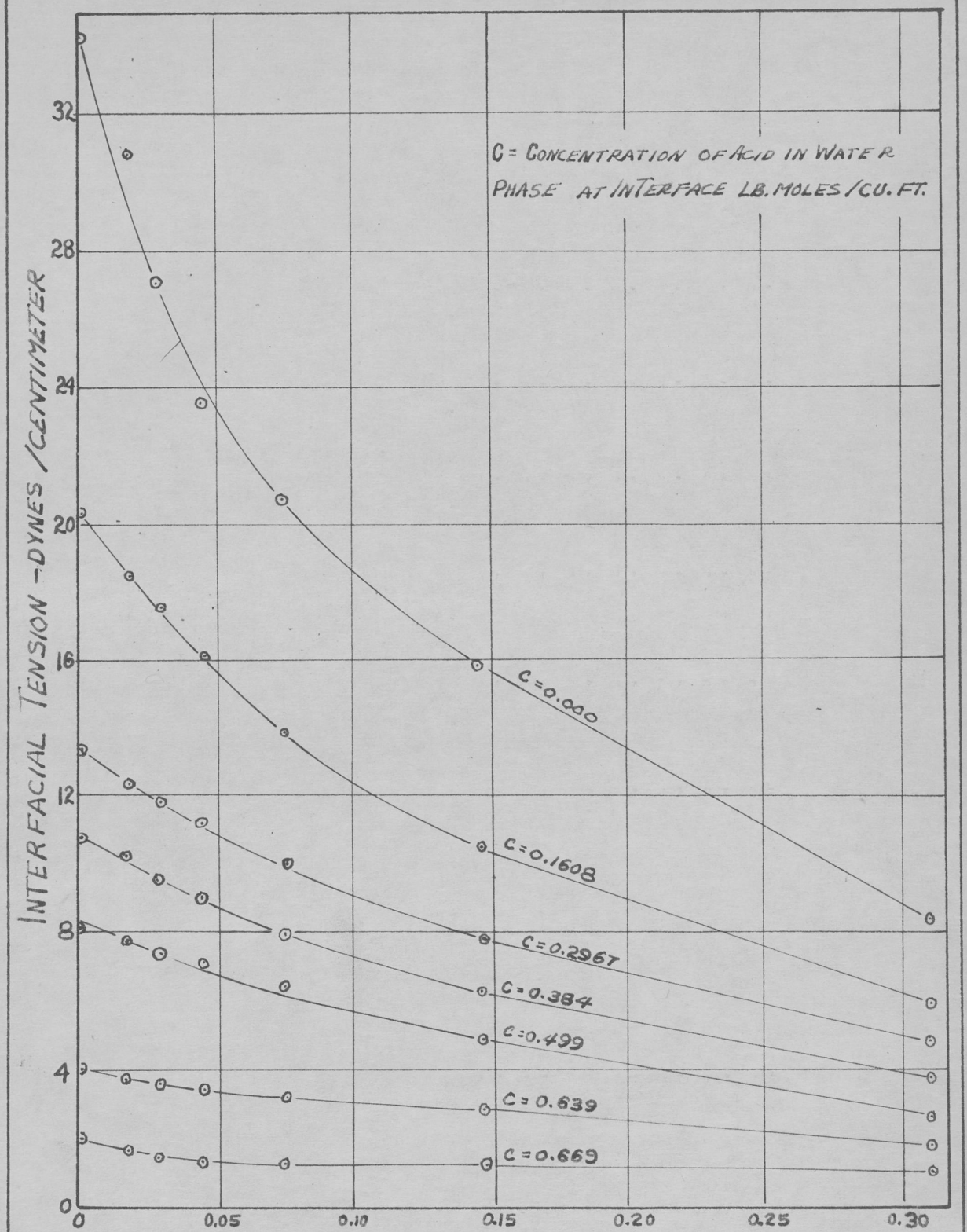

Fig. 10 Interfacial Tension of the Benzene-Acetic Acid-Water System
83±2°F

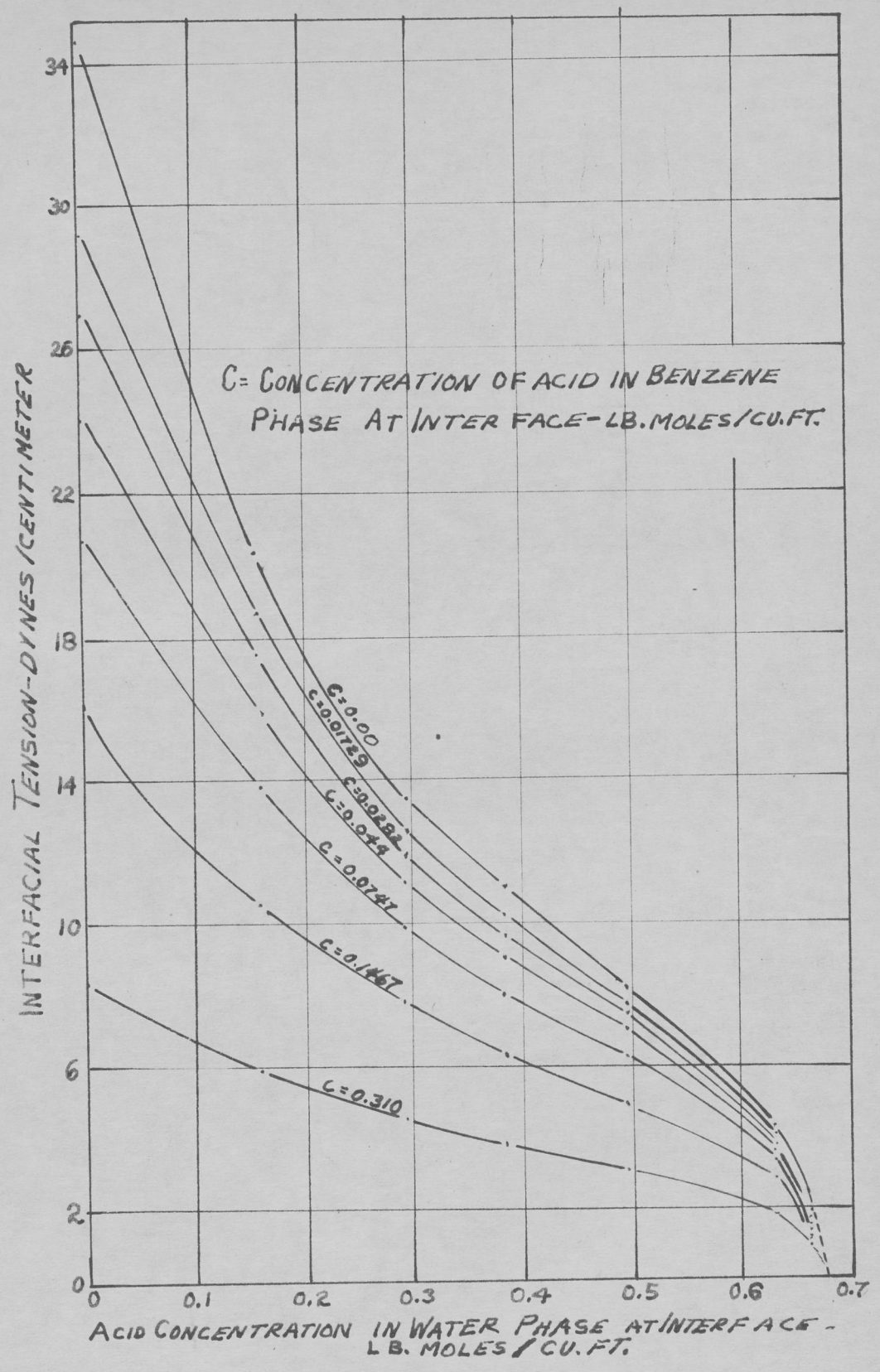

FIG. 11 INTERFACIAL TENSION OF THE BENZENE-ACETIC ACID-WATER SYSTEM 83±2°

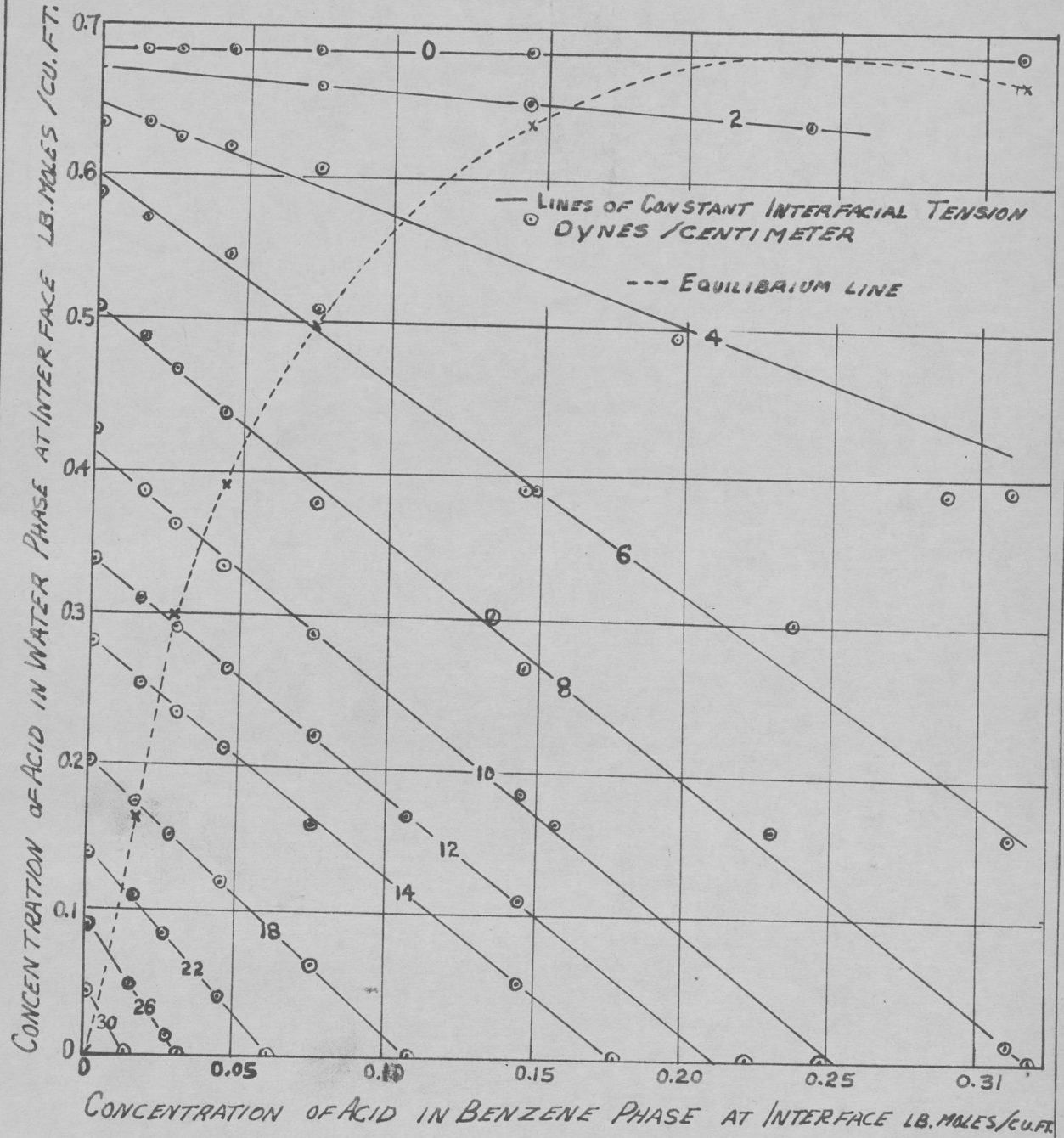

FIG. 12 INTERFACIAL TENSION OF THE BENZENE-ACETIC ACID - WATER SYSTEM 83 ± 2°F.

TABLE VI

EQUILIBRIUM DISTRIBUTION AND SPECIFIC GRAVITIES

Methyl Isobutyl Ketone - Acetic Acid - Water

83°F ± 2°

Water Phase		Ketone Phase	
Specific Gravity	Acid Concentration lb. mols/cu. ft.	Specific Gravity	Acid Concentration lb. mols/cu. ft.
0.9981	0.00	0.7931	0.000
0.9980	0.01365	0.7989	0.00666
1.0002	0.0504	0.8066	0.02735
1.0056	0.0974	0.8164	0.0565

TABLE VII

EXPERIMENTAL DATA: APPARENT INTERFACIAL TENSION VS TIME

Methyl Isobutyl Ketone - Acetic Acid - Water

Legend: c = Initial acid concentration in the ketone phase, lb. moles/cu. ft.
w = Initial acid concentration in the water phase, lb. moles/cu. ft.
t = Time of reading in seconds from the addition of the ketone phase
x = The apparent interfacial tension measurement, dynes/centimeter

c = 0.000 w = 0.000		c = 0.00666 w = 0.000		c = 0.02735 w = 0.000		c = 0.0565 w = 0.000		c = 0.000 w = 0.01365		c = 0.00666 w = 0.01365	
t	x	t	x	t	x	t	x	t	x	t	x
20	10.9	10	10.7	15	9.8	10	8.2	15	10.4	15	10.1
60	10.9	30	10.7	40	9.9	20	8.3	40	10.4	35	10.1
90	10.9	60	10.8	65	9.9	45	8.4	60	10.3	45	10.0
		90	10.8	90	10.0	60	8.6	85	10.3	70	9.9
		150	10.8	120	10.1	75	8.7	120	10.2	90	9.9
		180	10.8	160	10.1	100	8.7	145	10.2	110	9.8
						140	8.8	180	10.2	140	9.7
						180	8.9			180	9.7

c = 0.02735 w = 0.01365		c = 0.0565 w = 0.01365		c = 0.000 w = 0.0504		c = 0.00666 w = 0.0504		c = 0.02735 w = 0.0504		c = 0.0565 w = 0.0504	
t	x	t	x	t	x	t	x	t	x	t	x
20	9.4	10	8.0	10	9.1	20	8.9	20	8.3	10	7.3
35	9.4	25	8.1	30	9.0	35	8.9	50	8.3	30	7.4
50	9.5	40	8.3	40	9.0	50	8.9	75	8.4	40	7.6
70	9.4	65	8.6	60	8.9	75	8.9	90	8.2	65	7.7
95	9.5	90	8.8	85	8.9	95	8.8	120	8.2	90	7.8
125	9.6	120	8.9	120	8.8	135	8.7	155	8.2	115	7.8
160	9.6	160	9.0	160	8.8	165	8.7			140	7.9
										180	7.9

TABLE VII (continued)

EXPERIMENTAL DATA: APPARENT INTERFACIAL TENSION VS TIME

Methyl Isobutyl Ketone - Acetic Acid - Water

Legend: c = Initial acid concentration in the ketone phase, lb. moles/cu. ft.
w = Initial acid concentration in the water phase, lb. moles/cu. ft.
t = Time of reading in seconds from the addition of the ketone phase
x = The apparent interfacial tension measurement, dynes/centimeter

c = 0.000 w = 0.0974		c = 0.00666 w = 0.0974		c = 0.02735 w = 0.0974		c = 0.0565 w = 0.0974	
t	x	t	x	t	x	t	x
20	7.5	10	7.3	5	7.1	15	6.5
35	7.6	30	7.4	25	7.3	50	6.5
50	7.8	45	7.6	45	7.4	85	6.5
75	7.8	60	7.6	60	7.5	120	6.4
105	7.9	90	7.7	90	7.4	180	6.5
135	8.0	120	7.8	120	7.6		
180	8.1	160	7.9	150	7.5		
				180	7.5		

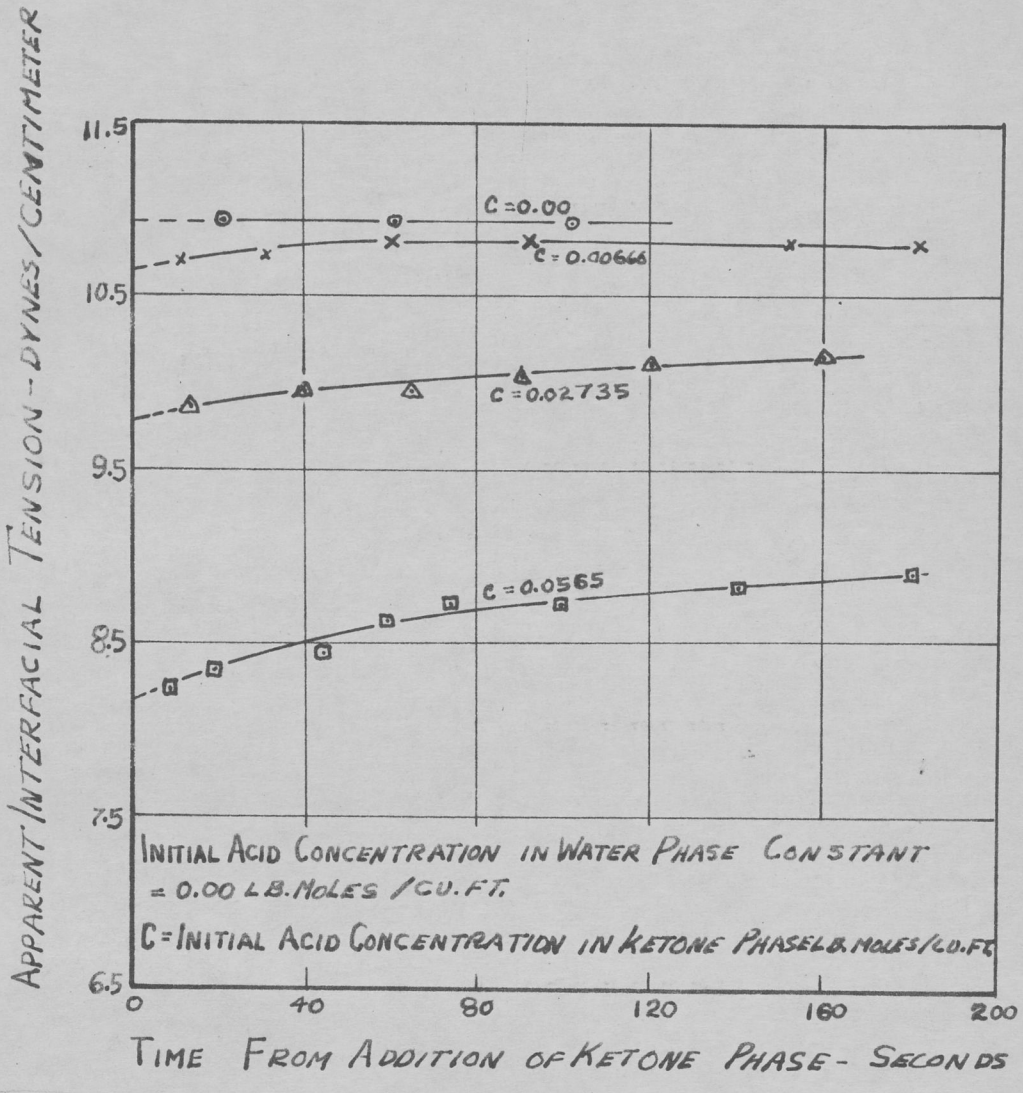

FIG. 13 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME FOR THE METHYL ISOBUTYL KETONE – ACETIC ACID - WATER SYSTEM 83 ± 2°F

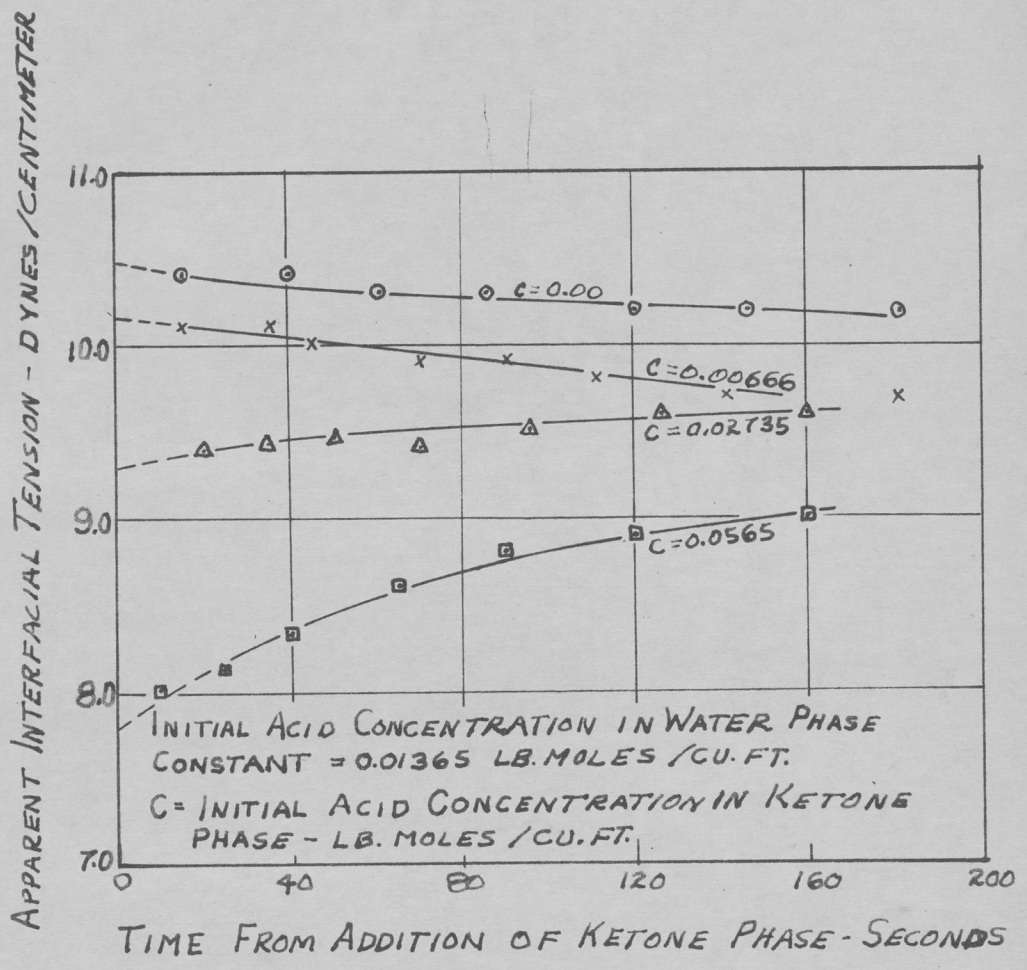

FIG. 14 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME FOR THE SYSTEM METHYL ISOBUTYL KETONE ACETIC ACID - WATER 83±2°F

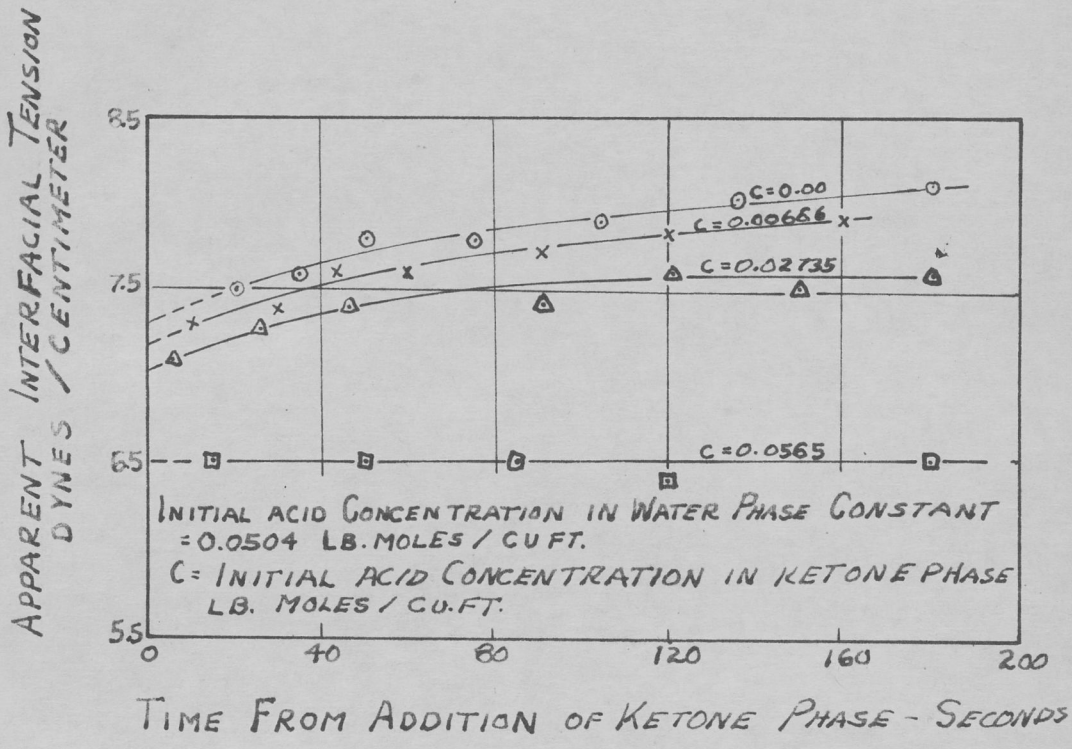

FIG. 15 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME FOR THE SYSTEM METHYL ISOBUTYL KETONE-ACETIC ACID-WATER SYSTEM 83 ± 2 °F

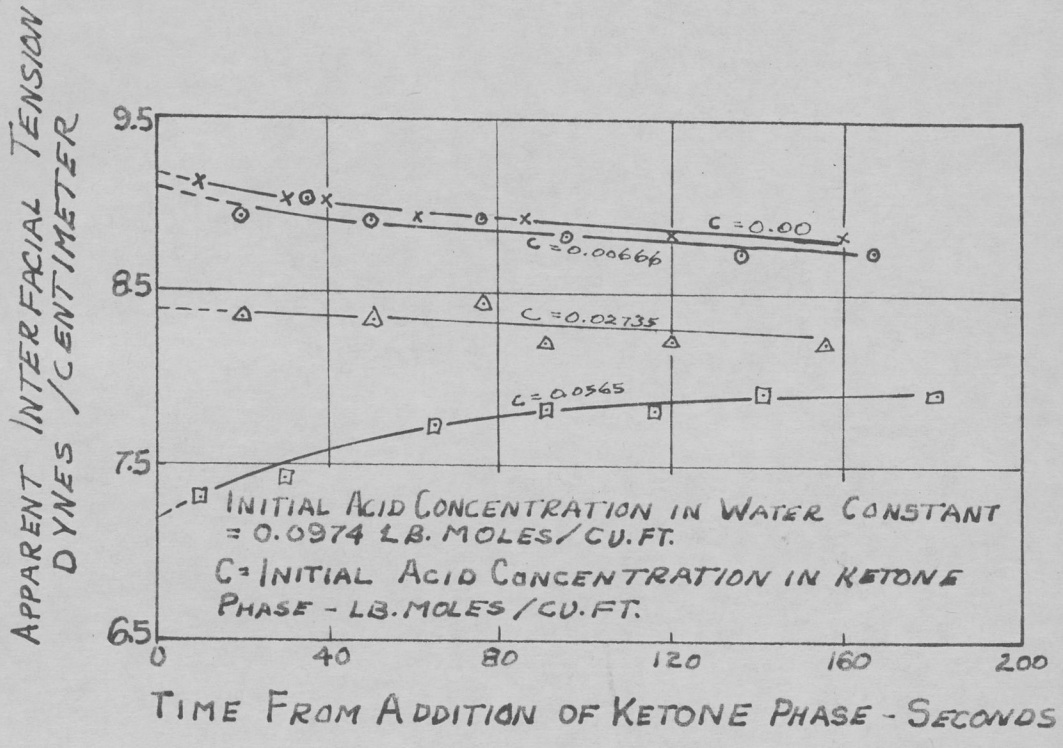

FIG. 16 VARIATION OF APPARENT INTERFACIAL TENSION WITH TIME FOR THE SYSTEM METHYL ISOBUTYL KETONE - ACETIC ACID - WATER 83 ± 2°F

TABLE VIII

APPARENT INTERFACIAL TENSION

Methyl Isobutyl Ketone - Acetic Acid - Water

Dynes/centimeter

Acid Concentration in the Water Phase lb. moles/cu. ft.	Acid concentration in the Ketone Phase lb. moles/cu. ft.			
	0.000	0.00666	0.02735	0.0565
0.000	10.9	10.65	9.75	8.1
0.01365	10.45	10.17	9.3	7.8
0.0504	9.15	9.0	8.35	7.15
0.0974	7.30	7.22	7.05	6.5

TABLE IX

INTERFACIAL TENSION CORRECTION FACTOR

Methyl Isobutyl Ketone - Acetic Acid - Water

Acid Concentration in the Water Phase lb. moles/cu. ft.	Acid concentration in the Ketone Phase lb. moles/cu. ft.			
	0.000	0.00666	0.02735	0.0565
0.000	0.9114	0.9116	0.909	0.9012
0.01365	0.908	0.9081	0.9055	0.8971
0.0504	0.9011	0.9015	0.90	0.895
0.0974	0.8891	0.890	0.8906	0.889

TABLE X

TRUE INTERFACIAL TENSION

Methyl Isobutyl Ketone - Acetic Acid - Water

Dynes/centimeter

Acid Concentration in the Water Phase lb. moles/cu. ft.	Acid concentration in the Ketone Phase lb. moles/cu. ft.			
	0.000	0.00666	0.02735	0.0565
0.000	10.0	9.7	8.9	7.3
0.01365	9.5	9.2	8.4	7.0
0.0504	8.3	8.1	7.5	6.4
0.0974	6.5	6.4	6.3	5.8

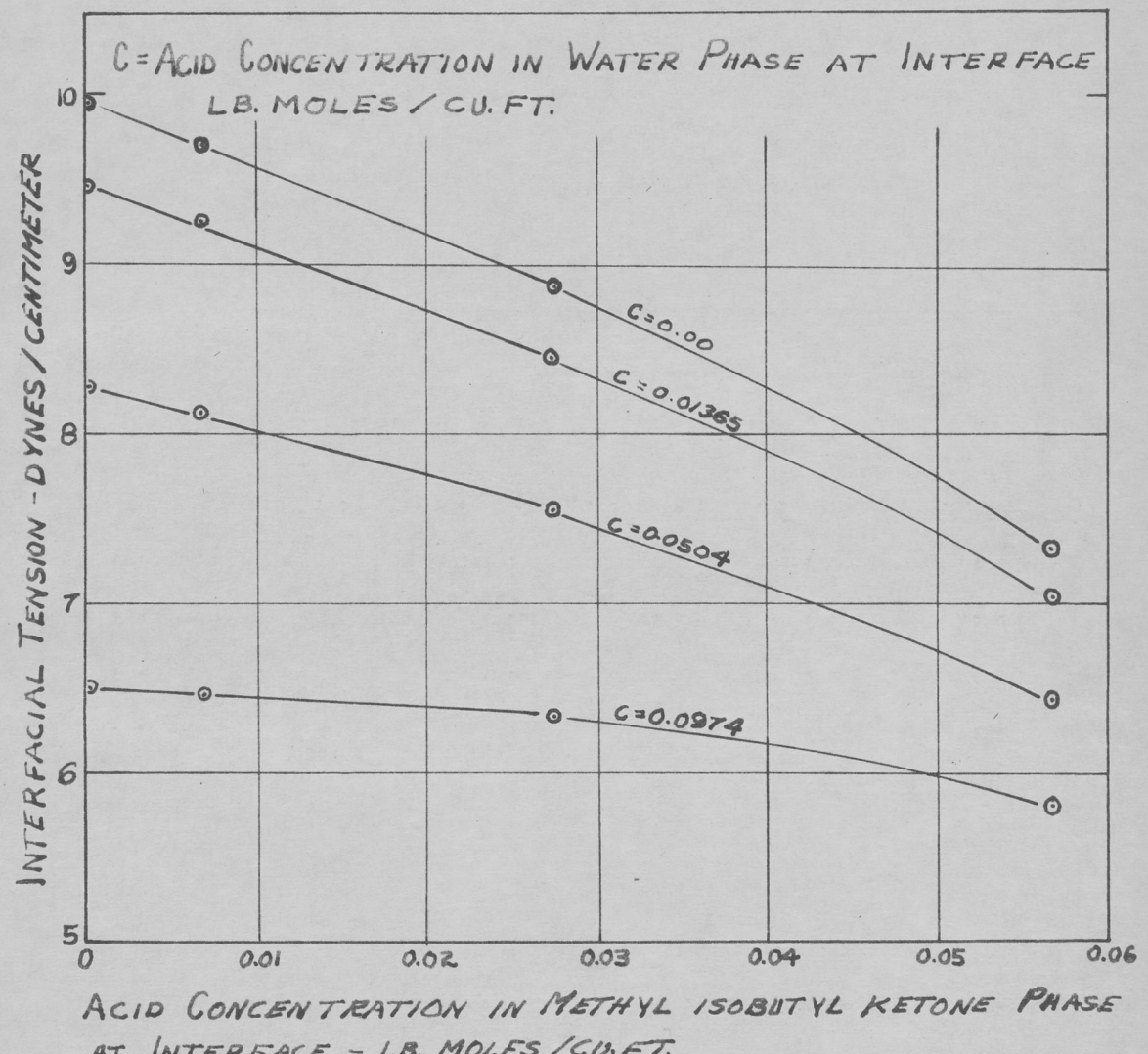

Fig. 17 Interfacial Tension of the Methyl isobutyl Ketone - Acetic acid - Water System 83 ± 2°F

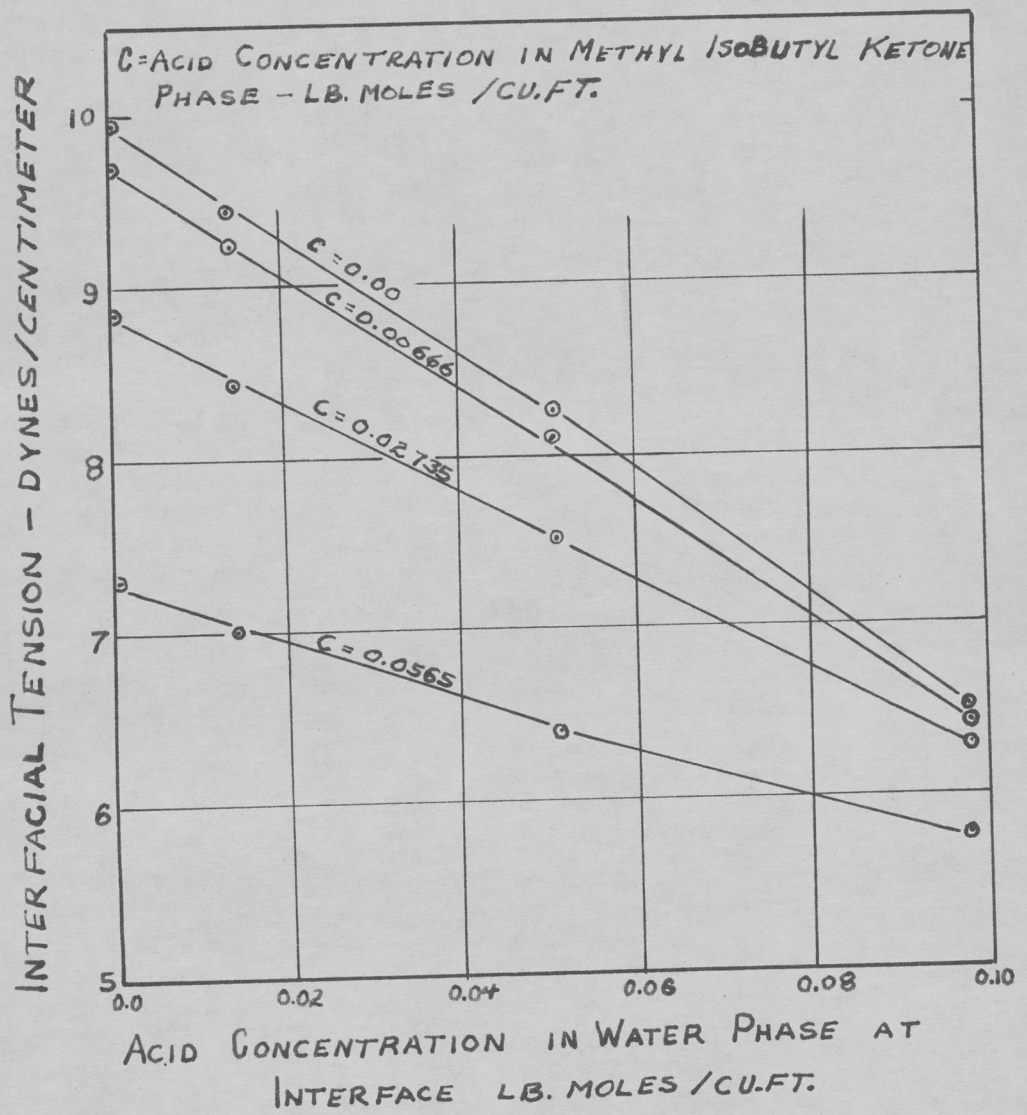

Fig. 18 Interfacial Tension of the System Methyl Isobutyl Ketone - Acetic Acid - Water 83±2°F

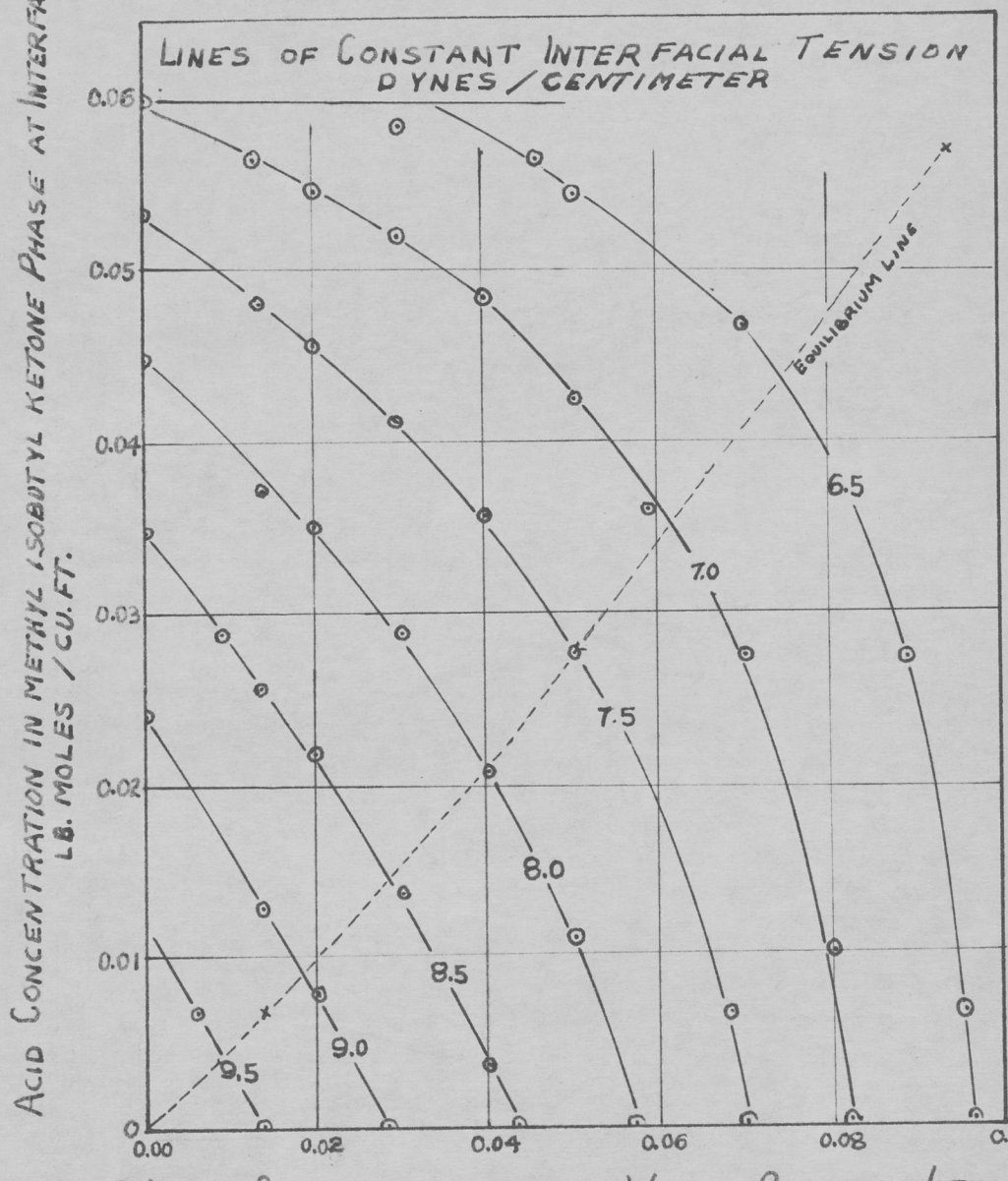

FIG. 19 INTERFACIAL TENSION OF THE METHYL ISOBUTYL KETONE–ACETIC ACID–WATER SYSTEM 83 ± 2°F

DISCUSSION OF RESULTS

The final results of this report are given in Figures 12 and 19 which show lines of constant interfacial tension plotted on coordinates of acid concentrations at the interface in the two phases. These acid concentrations were based on overall concentrations of the initial solutions for the two phases, but these concentrations were assumed to be the same as those at the interface at the instant of the formation of the interface. In addition to the lines of constant interfacial tension, equilibrium curves were constructed from data given in Tables I and VI.

The only data available with which to compare results of this report are equilibrium data taken by Andreas on the methyl isobutyl ketone-acetic acid-water system. Andreas employed the pendant drop method in which the boundry tensions were calculated from measurements on large photographic images of the drops.[2] Values from his work were found to be from 10 to 20 per cent less than those found in this work. Andreas reported a value of 8.8 dynes per centimeter for the methyl isobutyl ketone-water interface. This compared to a value of 10.0 found in this work. The difference between these measurements may be attributed to impurities in one or both of the systems.

The degree of accuracy of the measurements made was greatly affected by the acid concentrations in the two

systems. It was found that with high acid concentration in the benzene system, readings were very low. Data in general would probably have been better if measurements could have been made sooner after the addition of the lighter phase.

CONCLUSIONS AND RECOMMENDATIONS

Although the overall results of this investigation could not be checked with previous work, they should at least give an indication as to the magnitude of interfacial tensions at non-equilibrium conditions for the two systems. Since the interfacial tensions finally reported are given as a function of concentration at the interface in each phase, the data are not directly applicable to practical problems. Work should be done on the concentration gradient existing when diffusion takes place across a liquid-liquid interface.

If it is found that data procured by another method agree with those reported herein, then the ring method has been shown to provide a rapid method for obtaining data on interfacial tensions of non-equilibrium systems.

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APPENDIX

SAMPLE CALCULATIONS

(1) Standardization of sodium hydroxide solution:

weight of potassium acid phthalate = 2.3420 grams

molecular weight of potassium acid phthalate = 204.2

The sample of acid phthalate required 10.74 mls. of sodium hydroxide solution.

$$\text{normality of base} = \frac{2.3420 \times 1000}{204.2 \times 10.74} = 1.0638$$

Another sample gave the normality of 1.0632

Average value = 1.0635 gram moles/liter

(2) Titration of a solution of acetic acid in water:

A 10 milliliter portion of solution required 14.68 milliliters of standard base to reach the end point.

Concentration of acid in the water phase

$$= \frac{14.68 \text{ ml}}{10.00 \text{ ml}} \times \frac{1.0635 \text{ gr. moles}}{\text{liter}} \times \frac{28.32 \text{ liters}}{\text{cu. ft.}} \times \frac{1 \text{ lb mole}}{453.6 \text{ gr mole}}$$

$$= 0.0974 \frac{\text{lb moles}}{\text{cu. ft.}}$$

(3) The calculation of true interfacial tension:

From Figure 14 the extrapolated value of apparent interfacial tension for the case of the water phase containing 0.01365 lb. moles acid/cu. ft. and the ketone phase containing 0.0565 lb. moles/cu. ft. the zero time intercept was found to be 7.8 dynes/centimeter. The difference in their specific gravity

measurements from Table VI was 0.9980-0.8164 = 0.1816. The specific gravity for water was 0.9951. The accepted value for water at 83°F = 0.9971. Therefore the difference in density would be 0.1816 x 0.9971/0.9951. The correction factor is a function of the apparent interfacial tension divided by the difference in density, 7.8 x 0.9951/0.1816 x 0.9971 = 42.9. From Figure 20 the correction factor was 0.8971. The true interfacial tension = 0.8971 x 7.8 = 7.0 dynes per centimeter.

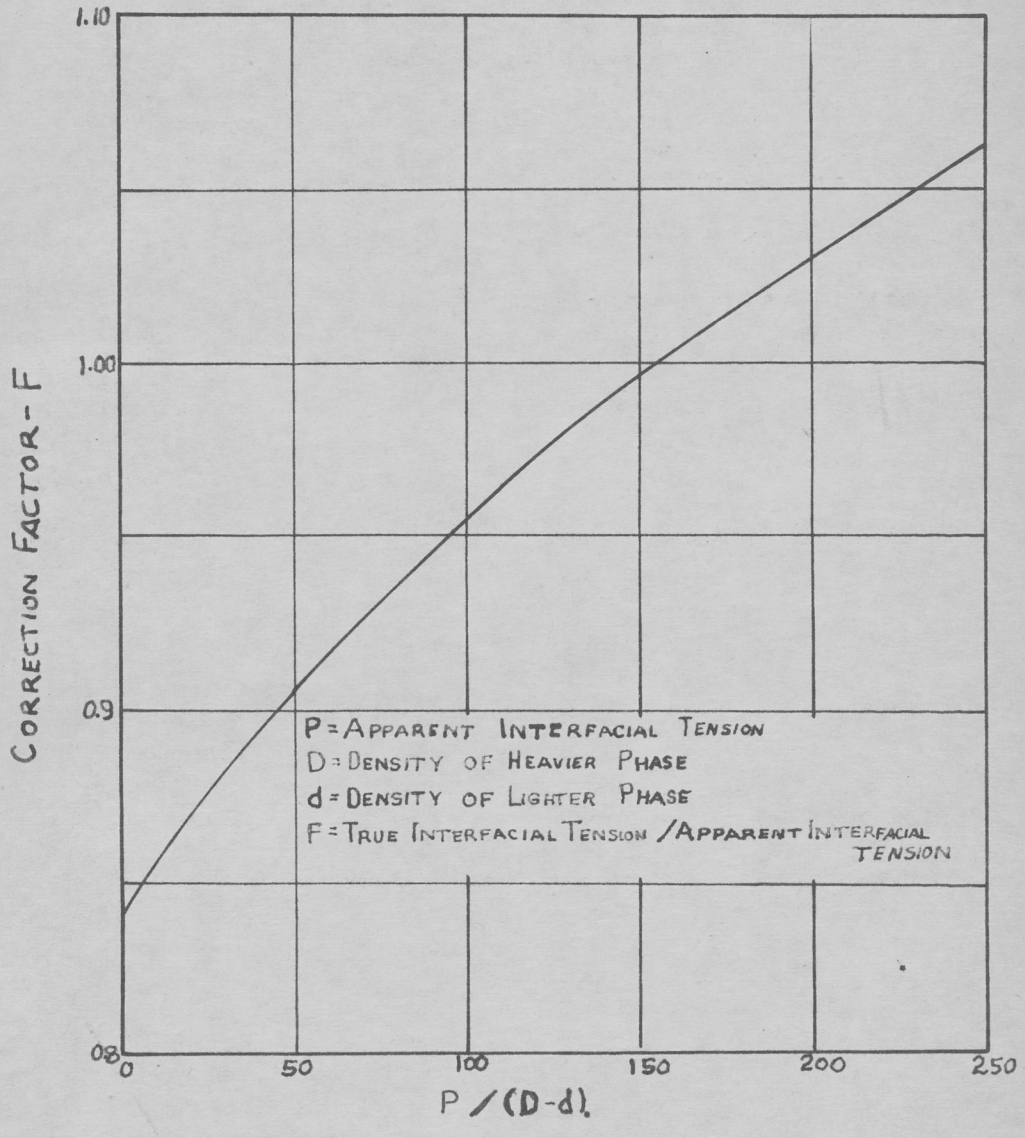

FIG. 20 CORRECTION CURVE FOR INTERFACIAL TENSION MEASUREMENT BY RING METHOD

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval that the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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Title Asst. Prof. Chem. Eng.

Date May 31, 1950