INTERFACIAL TENSION IN NON-EQUILIBRIUM SYSTEMS

PENDANT DROP METHOD

A THESIS

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SUMMARY

Interfacial tension in the benzene-acetic acid-water system under conditions of non-equilibrium has been investigated by means of the pendant drop method.

The method involved analysis of drops by a photographic technique. Characteristic measurements could be taken from an enlarged image of the drop which could be used to compute the apparent interfacial tension. The calculation method used was based on a force balance around the drop which included interfacial tension.

The photographs were taken with an Exata VX 35 mm reflex camera using Kodak Tri-x panchromatic film. The drops were formed by injecting the water phase through a stainless steel knife-edge tip by means of a hypodermic syringe. The drops, in most cases, were formed in the benzene phase which was contained in a test tube. Around the tube was a water filled outer jacket with flat glass sides which was designed to reduce distortion of the image.

Seven mixtures of benzene ranging from 0 to 0.0403 lb. moles/cu.ft. and seven mixtures of water and acetic acid with acid concentrations ranging from 0 to 0.3676 lb. moles/cu.ft. were combined to give a series of 49 runs. Series of photographs were taken of the drops at times ranging from 2 to 300 seconds from the instant of formation, and apparent interfacial tensions at these time intervals were computed for each of the 49 combinations. The interfacial tensions were plotted as a function of time and extrapolated to zero time in an attempt to determine the interfacial tension at time of initial contact of the phases. The extrapolated values of apparent interfacial tension at zero time were then correlated by plotting them as a function of the initial acid

concentration in the two phases. A final correlation of results was made by plotting lines of constant interfacial tension on coordinates of acid concentration in the two phases.

The resulting interfacial tensions in general were higher than those obtained by Collins for the benzene-acetic acid-water system.[2] The value obtained for pure benzene-water interfacial tension was 40.83 dynes/cm. The interfacial tension vs. time curves exhibited a definite wave characteristic which may be due to momentum of the drop or some uneven surface effects.[4]

It is recommended that the pendant drop method may be used with further refinements. A motion picture study of the drop might prove of value.

INTRODUCTION

In liquid-liquid extraction, correlation is frequently achieved by means of capacity coefficients. The capacity coefficient is the product of an area and a diffusion rate. To separate the terms, the drop sizes must be estimated so the total area over which diffusion takes place can be calculated. The individual drop sizes probably depend on distributor design, flow rate through the distributor, viscosities, densities and interfacial tension. The drops are formed while the solute being extracted is not in equilibrium between the two phases. One of the most important factors in determining the shape and size of the drop is interfacial tension.

The present work was initiated to check previous experimental work on interfacial tension in non-equilibrium systems by an independent method.[2†]

The method used for this work was that of the pendant drop. Photographs were made of drops and a method of attack similar to that used by Andreas for equilibrium systems was employed in determining the interfacial tension.[1] The system studied was benzene-acetic acid-water. Another study is being made on the system methyl isobutyl ketone-acetic acid-water using the same method.

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† Refer to references in bibliography.

THEORY

The method of attack which was used for the determination of interfacial tensions in non-equilibrium liquid-liquid systems at the time of contact was based on the method of pendant drops described for equilibrium systems by Andreas, Hauser and Tucker.[1]

The following basic equations are used in the analysis of a static pendant drop:

$$\Delta p = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \frac{2\sigma}{b} - \frac{g}{g_c}\left(\rho_d - \rho_c\right) z \qquad (1)$$

Where: Δp = pressure differential between dispersed and continuous phase.

σ = interfacial tension.

r_1 & r_2 = principal radii of curvature.

b = radius of curvature of drop at origin. (Origin is bottom of drop.)

ρ_d = density of dispersed phase.

ρ_c = density of continuous phase.

g = acceleration of gravity.

g_c = conversion factor.

z = vertical coordinate.

The expansion for r_1 is:

$$\frac{1}{r_1} = \frac{\dfrac{d^2z}{dx^2}}{\left[1 + \left(\dfrac{dz}{dx}\right)^2\right]^{3/2}} \qquad (2)$$

Where: x = horizontal distance from center of nozzle.

and for r_2:

$$\frac{1}{r_2} = \frac{\frac{dz}{dx}}{x\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}} \tag{3}$$

Substituting the values for r_1 and r_2 as expressed in equations (2) and (3) in equation (1) and simplifying gives:

$$\frac{d^2z}{dx^2} + \frac{\frac{dz}{dx}}{x}\left[1 + \left(\frac{dz}{dx}\right)^2\right] = \left[\frac{2}{b} - \frac{g}{g_c}\frac{(\rho_d - \rho_c)z}{\sigma}\right]\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2} \tag{4}$$

Equation (4) is a second-order, second-degree differential equation whose solution is unknown.

If we let $X = \frac{x}{b}$, $Z = \frac{z}{b}$, $Z' = \frac{dZ}{dX}$, $Z'' = \frac{d^2Z}{dX^2}$

and set

$$\beta = \frac{g}{g_c}\frac{(\rho_d - \rho_c)b^2}{\sigma} \tag{5}$$

the equation is reduced to a dimensionless form with b as unit length, which is:

$$Z'' + \frac{Z'}{X}\left[1 + (Z')^2\right] = \left[2 - \beta Z\right]\left[1 + (Z')^2\right]^{3/2} \tag{6}$$

The two parameters $(\rho_d - \rho_c)$ and β identify the drop represented by the equation.

By rearranging equation (5), σ may be expressed as a function of the parameters β and b and the specific weight $\frac{g}{g_c}(\rho_d - \rho_c)$.

Equation (5) may be rearranged so the parameters can be measured easily and accurately. The shape of the drop can be described by using the ratio of two diameters. If one diameter is in the plane at the equator and the other is taken at a distance from the bottom of the drop equal to the equatorial

diameter, the shape is described by:

$$s = \frac{d_s}{d_e} \tag{7}$$

Where: d_s = diameter at the selected plane as shown in Fig. 1.

d_e = diameter at the equator.

A third quantity (in addition to β and s) which is a function of the drop shape is the ratio of the diameter at the equator to the radius of curvature at the origin. We can define a new quantity:

$$H = \beta\left(\frac{d_e}{b}\right)^2 \tag{8}$$

which is a function of s.

Combining equations (5) and (8) and solving for boundary tension gives:

$$\sigma = \frac{g}{g_c}\,\frac{(\rho_d - \rho_c)\,b^2}{\beta} = \frac{g}{g_c}\,\frac{(\rho_d - \rho_c)\,d_e^2}{\beta\left(\frac{d_e}{b}\right)^2} = \frac{g}{g_c}\,\frac{(\rho_d - \rho_c)(d_e)^2}{H} \tag{9}$$

Using Table I, in which s is tabulated as a function of 1/H, the boundary tension may be computed from a photograph of the pendant drop.

It is possible to evaluate s as a function of 1/H mathematically by use of finite increments or series. However, an empirical evaluation is feasible and adequate. Table I was prepared by Andreas and Associates[1] by using various sized drops of conductivity water with a known surface tension of 72.0 dynes per centimeter at 25°C. The function has been checked and found to agree with the theoretical curves.

Using the above method to determine the values of interfacial tension as a function of time, an extrapolation may be made to zero time in order to determine the interfacial tension at the instant of contact.

TABLE I

ARITHMETIC TABULATION OF H-S FUNCTION FOR PENDANT DROPS

(Andreas, Hauser, & Tucker[1])

$\frac{1}{H}$

S	0	1	2	3	4	5	6	7	8	9
0.70	0.797	0.795	0.792	0.790	0.787	0.785	0.782	0.780	0.777	0.775
0.71	0.772	0.770	0.767	0.765	0.762	0.759	0.757	0.754	0.752	0.749
0.72	0.747	0.744	0.742	0.739	0.737	0.735	0.732	0.730	0.727	0.725
0.73	0.722	0.720	0.718	0.715	0.713	0.711	0.709	0.706	0.704	0.702
0.74	0.699	0.697	0.695	0.692	0.690	0.688	0.685	0.683	0.681	0.679
0.75	0.676	0.674	0.672	0.670	0.668	0.665	0.663	0.661	0.659	0.657
0.76	0.655	0.652	0.650	0.648	0.646	0.644	0.642	0.640	0.637	0.635
0.77	0.633	0.631	0.629	0.627	0.625	0.623	0.621	0.619	0.617	0.615
0.78	0.613	0.611	0.609	0.607	0.605	0.603	0.601	0.599	0.597	0.595
0.79	0.593	0.591	0.589	0.587	0.585	0.583	0.581	0.579	0.577	0.575
0.80	0.573	0.571	0.570	0.568	0.566	0.564	0.562	0.561	0.559	0.557
0.81	0.555	0.553	0.551	0.550	0.548	0.546	0.544	0.542	0.540	0.539
0.82	0.537	0.535	0.533	0.532	0.530	0.528	0.526	0.524	0.523	0.521
0.83	0.519	0.518	0.516	0.515	0.513	0.511	0.509	0.507	0.506	0.504
0.84	0.502	0.501	0.499	0.498	0.496	0.494	0.493	0.491	0.490	0.488
0.85	0.486	0.485	0.483	0.482	0.480	0.479	0.477	0.476	0.474	0.473
0.86	0.471	0.470	0.468	0.467	0.465	0.464	0.462	0.461	0.459	0.458
0.87	0.457	0.455	0.454	0.452	0.451	0.450	0.448	0.447	0.446	0.444
0.88	0.443	0.441	0.440	0.439	0.437	0.436	0.434	0.433	0.431	0.430
0.89	0.429	0.428	0.426	0.425	0.423	0.422	0.420	0.419	0.418	0.417
0.90	0.415	0.414	0.413	0.411	0.410	0.409	0.408	0.406	0.405	0.404
0.91	0.403	0.401	0.400	0.399	0.398	0.396	0.395	0.394	0.393	0.391
0.92	0.390	0.389	0.388	0.386	0.385	0.384	0.383	0.382	0.381	0.379
0.93	0.378	0.377	0.376	0.375	0.373	0.372	0.371	0.370	0.369	0.368
0.94	0.366	0.365	0.364	0.363	0.362	0.361	0.359	0.358	0.357	0.356
0.95	0.355	0.354	0.353	0.352	0.351	0.350	0.349	0.348	0.346	0.345
0.96	0.344	0.343	0.342	0.341	0.340	0.339	0.338	0.337	0.335	0.334
0.97	0.333	0.332	0.331	0.330	0.329	0.328	0.327	0.326	0.325	0.324
0.98	0.323	0.322	0.321	0.320	0.319	0.318	0.317	0.316	0.315	0.314
0.99	0.313	0.312	0.311	0.310	0.309	0.308	0.307	0.306	0.305	0.304
1.00	0.303									

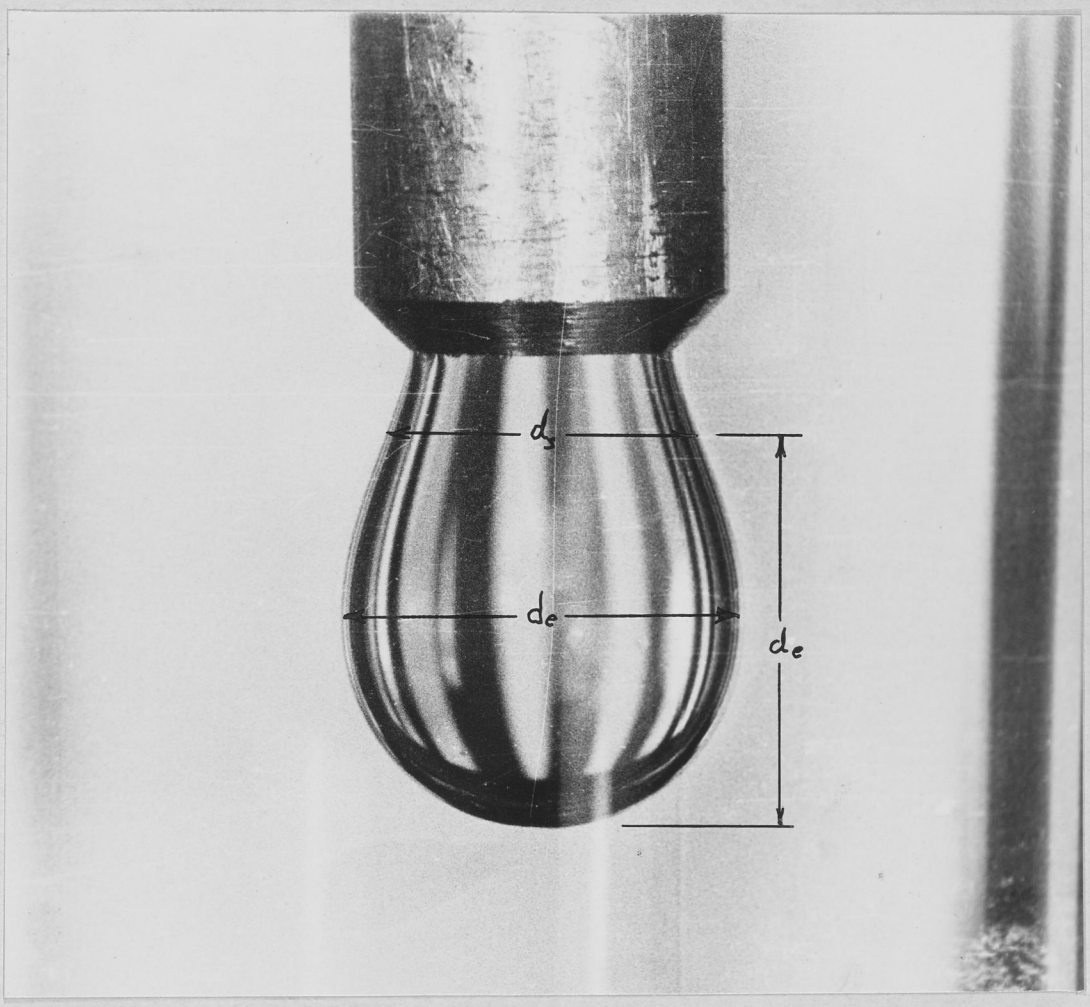

Figure 1. Enlarged photograph of drop showing principal dimensions.

MATERIAL AND EQUIPMENT

An Exata VX 35 mm reflex camera mounted on an adjustable tripod was used for making photographs of drops for interfacial tension measurements. A close-up attachment was used for further enlargement and better definition of the drop. Kodak Tri-x panchromatic film was used (ASA 160 - tungsten). The film was sufficiently fast to permit exposures of f-11 and 0.001 of a second. Two flood lights were used for lighting. The lights were used only when necessary to prevent over heating of the cell.

The cell used consisted of an outer jacket which was filled with water. This jacket comprised two parallel flat glass plates mounted between stainless steel sides, top, and bottom. Holes were provided in the top and bottom from previous work using this same jacket. The bottom hole was corked and a 65 mm pyrex tube containing the light phase was fitted through the top hole and secured with a ring stand. The heavy phase was then placed in a hypodermic syringe fitted with stainless steel knife edge tips approximately 17 inches long and 5.3 mm or 4.5 mm inside diameter. At the instant of formation of the drop an electric sweep-second hand timer was started and photographs were taken at known intervals from the time of formation.

The film was developed in Kodak DK-50 for eight minutes, washed, fixed for fifteen minutes, washed for twenty minutes and dried. A Da-brite tank was used for developing.

The individual frames were projected onto scaled paper. As a reference point, a piece of thermometer stem whose calibrations could be measured was photographed with the tip and suspended drop. The measure-

ments were taken with dividers. The results of the measurements are recorded in a University of Tennessee research record notebook pages 18157 to 18178.

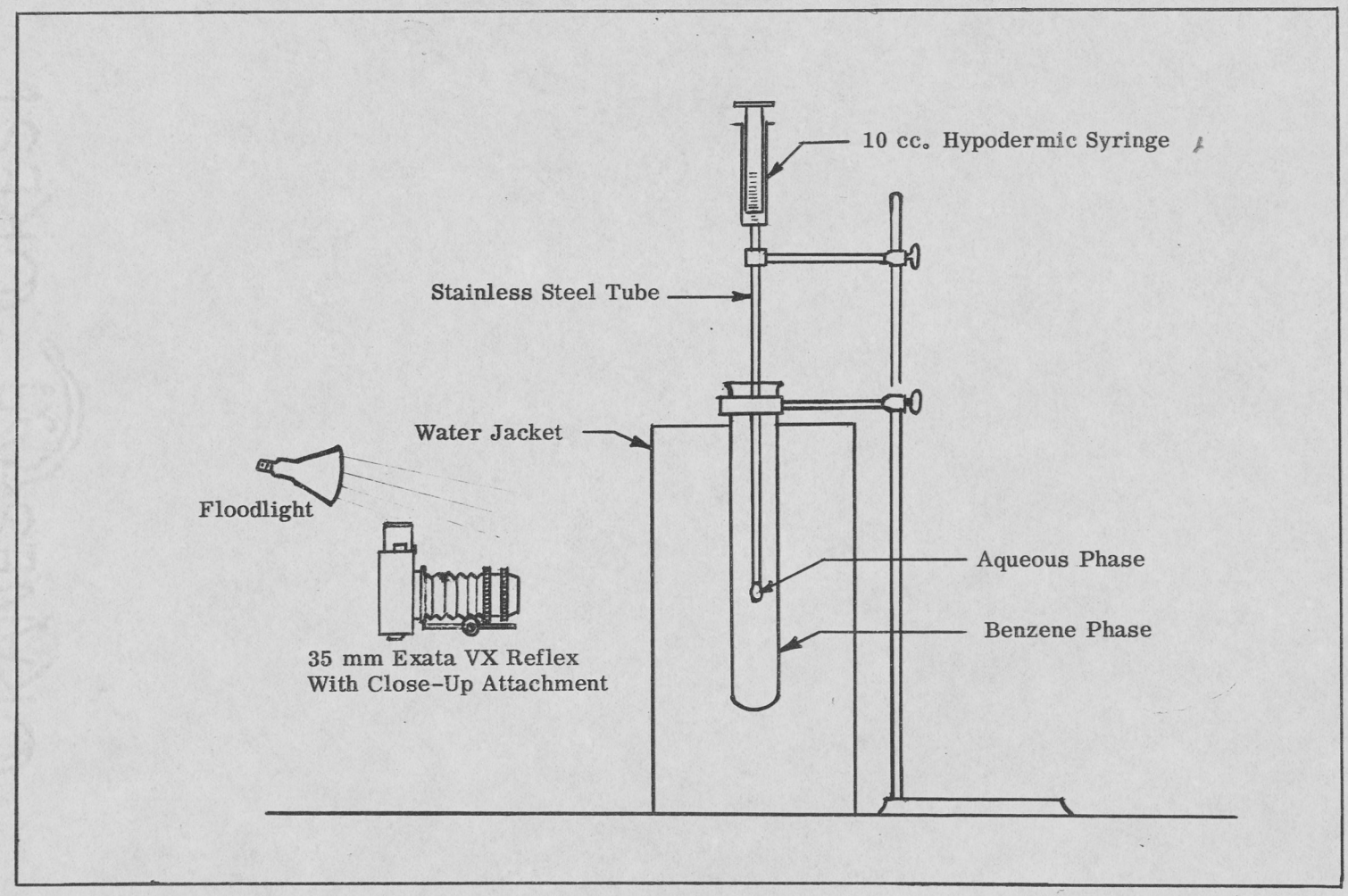

Figure 2. Sketch of Apparatus Used for Determinations of Interfacial Tensions in the Benzene-Acetic Acid-Water System.

TABLE II

EQUILIBRIUM DISTRIBUTION AND SPECIFIC GRAVITIES
BENZENE-ACETIC ACID-WATER
77°F

Water Phase		Benzene Phase	
Specific Gravity	Acid Concentration lb. moles/cu.ft.	Specific Gravity	Acid Concentration lb. moles/cu.ft.
0.9991	0.0000	0.8728	0.0000
1.0160	0.1350	0.8739	0.0069
1.0259	0.2080	0.8752	0.0153
1.0307	0.2510	0.8759	0.0211
1.0380	0.3277	0.8772	0.0332
1.0387	0.3348	0.8774	0.0344
1.0409	0.3676	0.8779	0.0403

PROCEDURE

The material and equipment mentioned in the preceding section was set up and used in the following manner. Drum grade benzene was found to be sufficiently contaminated to warrant a reflux distillation with a partial takeoff. It is estimated that this reflux ratio was about 50:1. After distillation the benzene was mixed with an equal amount of distilled water and various amounts of acetic acid. Seven different acetic acid concentrations were used ranging initially from 0 to approximately 0.4 pound mole per cubic foot in the water phase. After equilibrium was attained the two phases were separated and titrated against standard sodium hydroxide solutions to determine the acid concentration. The density of each phase was determined on a Westphal balance. All interfacial tension measurements and density measurements were carried out at a constant temperature of 77°F (air conditioned room).

A series of tests was made with the apparatus set up as shown in Fig. 2 to find the correct lighting, the shutter speed and opening, and the distance from drop to camera best suited for the experimental work. It was found that a distance of six to eight inches from the end of the close up lens to the drop was adequate. These tests also served as a check on the validity of the method since mixtures of known surface tension such as carbon tetrachloride-water were used and back checked. Another series of tests was made to determine the tip size best suited for the needs. This was done by running the benzene system with various size tips to find the d_s/d_e ratio that would fall within the limits set up in Table I.

Moving from the preliminary work to the actual determinations

the following method of attack was developed. The heavier phase in the 10 cc hypodermic syringe was placed into the lighter phase in the test tube and a drop formed at the tip. (See Fig. 1). The 15 inch stainless steel knife edge tips were held in place by a burette clamp which gave the desired stability and the necessary ease of handling. The test tube was placed in a water filled outer jacket with flat glass which reduced distortion of the image. Four runs were made with an inverted tip, the heavy phase being in the test tube and the lighter phase in the hypodermic syringe. These tests were made in an attempt to check the theoretical ideas that stipulate that the position of the drop has no effect upon the interfacial tension.

Time zero was taken as the time when drop formation began. Frequently it became necessary to discharge one or two drops before a drop of the proper size could be obtained. A series of pictures was taken at known intervals until equilibrium was approximated. The above attack was used on all forty-nine concentration combinations of the benzene-acetic acid-water system.

A filmstrip projector was used to further magnify the drop. The measurements of d_s and d_e were taken from the photograph as shown in Fig. 1. These measurements were subsequently used to calculate the interfacial tension.

RESULTS

The results obtained for interfacial tension measurements on the benzene-acetic acid-water system are summarized in the following figures and tables.

Table II gives the equilibrium distribution of acetic acid in the two phases with corresponding densities. Tables III to IX show data which were taken and calculated from the drop characteristics for each of seven series in which the acetic acid concentration in the benzene phase was held constant and the acetic acid concentration in the water phase was varied using seven different concentrations. Fig. 3 to 9 are plots of interfacial tension vs. time for constant acid concentration in the benzene phase corresponding to Tables III to IX.

Table X shows data taken using four different combinations of the benzene-acetic acid-water system with an inverted tip in which the light phase drop was allowed to form upward into the heave phase. Fig. 10 is a plot of interfacial tension vs. time for the inverted tip.

Table XI shows the values of interfacial tension extrapolated to zero time. The values were determined from Fig. 3 to 9. These values were used in plotting Fig. 11 and 12. From Fig. 11 and 12, the final correlation of data was made in Fig. 13 which shows lines of constant interfacial tension plotted on coordinates of acid concentration in the two phases. For comparison, a plot of Collins data in the same range covered by Fig. 13 is included in Fig. 14.

Fig. 15 is an actual photograph of a drop showing the effects of mass transfer. This will be discussed in the section following the results.

TABLE III

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0000
ρ_c = Density of Benzene Phase = 0.8728 gms/cc
W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft.
Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	2	7.84	6.30	43.07
	10	7.85	6.29	43.56
	12	7.76	6.41	39.22
	25	7.85	6.30	43.33
	60	7.75	6.30	40.89
	120	7.65	6.20	40.14
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	2	6.55	5.00	39.00
	10	6.15	5.30	24.83
	25	6.15	5.25	25.46
	50	6.05	5.30	23.00
	95	6.00	5.10	24.55
	180	6.00	5.05	25.20
	240	5.80	5.40	24.55
	300	5.80	5.40	25.54
Run 3	W = 0.2080, ρ_d = 1.0259 gms/cc			
	5	5.40	5.20	14.92
	15	5.60	5.20	17.83
	30	5.60	5.20	17.83
	60	5.60	5.20	17.83
	120	5.55	5.05	17.33
	180	5.60	5.10	18.82
	240	5.60	5.10	18.82
	300	5.65	5.10	18.82
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	2	4.80	4.30	14.97
	10	4.80	4.25	15.54
	30	4.80	4.20	16.04
	60	4.80	4.20	16.04
	125	4.80	4.20	16.04
	180	4.65	4.20	13.75
	240	4.55	4.20	12.36
	300	4.50	4.15	12.16

TABLE III (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 gms/cc			
	4	4.70	4.40	13.27
	15	4.65	4.35	13.02
	25	4.80	4.50	13.76
	45	4.80	4.50	13.76
	60	4.85	4.50	14.51
	120	4.70	4.40	13.27
	180	4.60	4.40	11.96
	240	4.65	4.35	13.02
	300	4.70	4.30	14.16
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	3	4.55	4.30	12.15
	6	4.50	4.30	11.49
	10	4.50	4.25	11.92
	25	4.50	4.30	11.49
	40	4.50	4.25	11.92
	60	4.50	4.25	11.92
Run 7	W = 0.3676, ρ_d = 1.0409 gms/cc			
	3	4.55	4.15	13.64
	7	4.55	4.25	12.72
	15	4.45	4.15	12.23
	30	4.45	4.25	11.41
	60	4.40	4.20	11.58
	120	4.40	4.20	11.58
	195	4.45	4.30	11.02
	300	4.45	4.25	11.41

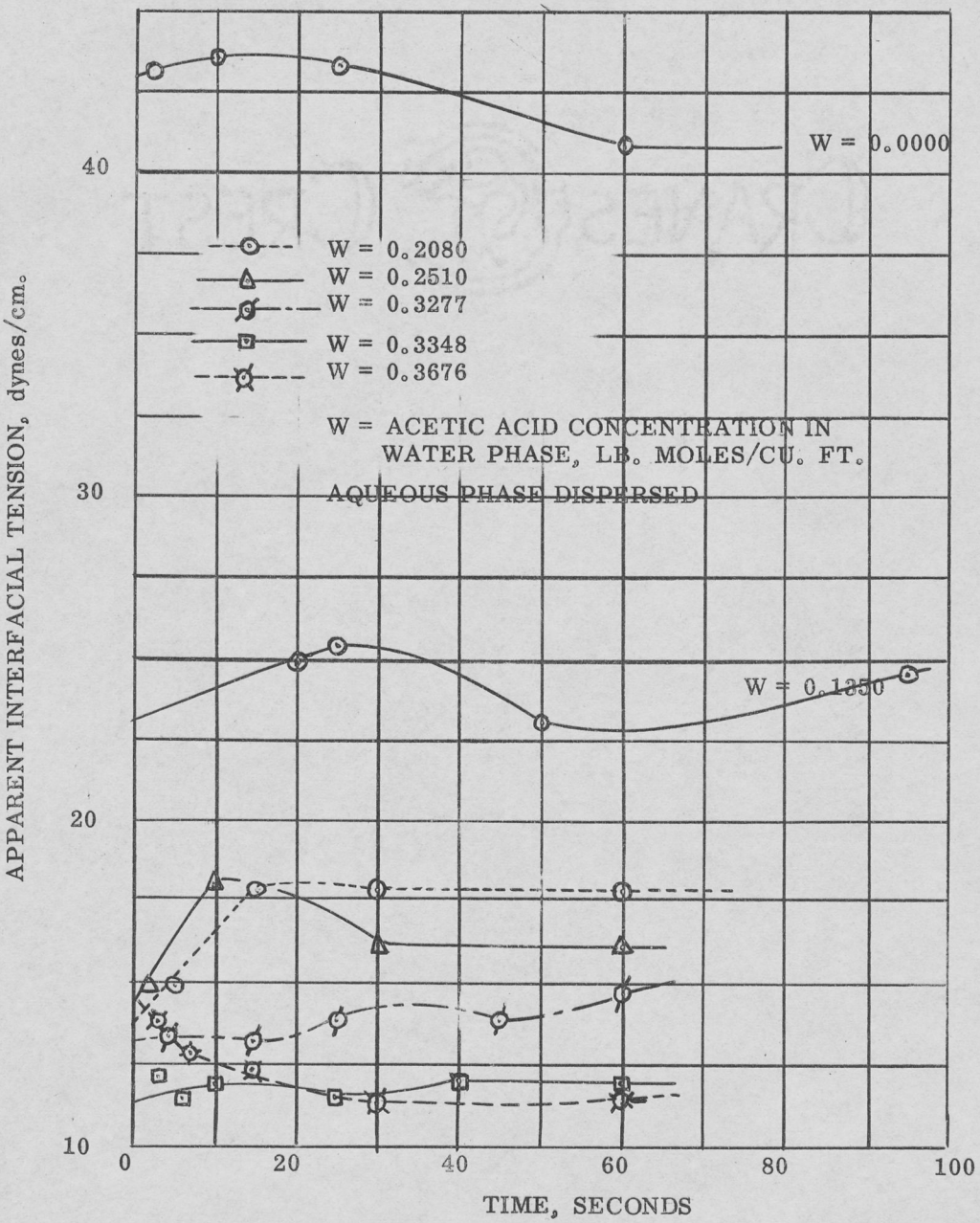

Figure 3. Plot of Interfacial Tension vs. Time for Benzene-Acetic Acid-Water System. Concentration of Acetic Acid in Benzene Phase Constant = 0.0000.

TABLE IV

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0060 Lb. Moles/Cu. Ft.
ρ_c = Density of Benzene Phase = 0.8739 gms/cc
W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft.
Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	6	8.16	6.18	54.00
	15	8.16	6.18	54.00
	23	8.16	6.25	52.45
	37	8.16	6.25	52.45
	60	8.10	6.25	50.64
	120	8.03	6.05	53.01
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	5	6.61	5.55	28.35
	6	6.76	5.69	31.76
	15	6.61	5.69	28.60
	40	6.68	5.69	27.86
	45	6.55	5.62	26.28
	300	6.48	5.62	25.02
Run 3	W = 0.2080, ρ_d = 1.0259 gms/cc			
	5	6.20	5.79	21.48
	10	6.06	5.60	21.06
	15	6.02	5.33	23.54
	25	6.24	5.83	21.64
	31	6.24	5.83	21.64
	60	6.24	5.79	20.02
	120	6.11	5.69	20.91
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	4	5.56	5.02	19.53
	10	5.56	5.02	19.53
	15	5.59	5.07	19.50
	30	5.54	4.98	19.67
	60	5.45	5.00	17.99
	120	5.45	5.02	17.76

TABLE IV (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 dynes/cc			
	3	5.21	5.04	14.71
	13	5.22	5.21	13.36
	16	5.31	5.17	14.92
	30	5.30	5.12	15.27
	60	5.30	5.21	14.45
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	3	5.12	4.79	15.75
	7	5.08	4.88	14.30
	20	5.21	4.97	15.38
	36	5.21	5.04	14.77
	60	5.29	5.12	15.14
	120	5.29	5.12	15.14
Run 7	W = 0.3676, ρ_d = 1.0409 gms/cc			
	4	4.96	4.91	16.71
	14	5.06	4.91	13.96
	21	5.04	4.96	13.26
	60	5.11	5.09	13.12
	195	5.16	4.98	14.06

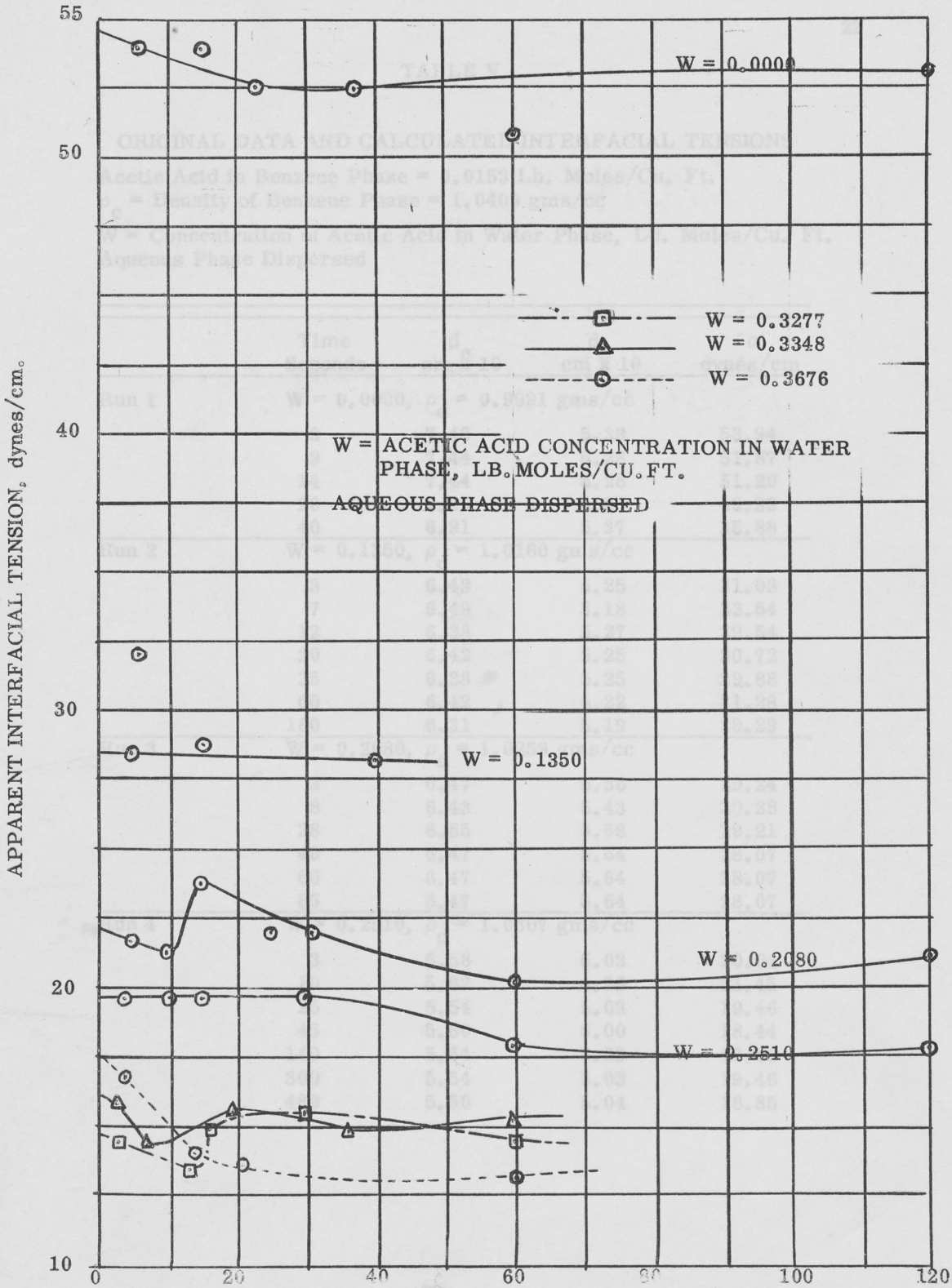

Figure 4. Plot of Interfacial Tension vs. Time for Benzene-Acetic Acid-Water System. Acetic Acid in Benzene Phase Constant = 0.0060 Lb. Moles/Cu. Ft.

TABLE V

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0153 Lb. Moles/Cu. Ft.
ρ_c = Density of Benzene Phase = 1.0409 gms/cc
W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft. Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	3	7.49	5.33	53.94
	9	7.44	5.28	51.87
	14	7.44	5.28	51.20
	20	7.39	5.33	49.33
	40	6.91	5.37	35.88
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	3	6.43	5.25	31.03
	7	6.49	5.18	33.54
	12	6.38	5.27	29.54
	20	6.42	5.25	30.72
	35	6.38	5.25	29.88
	60	6.42	5.22	31.28
	180	6.31	5.19	29.29
Run 3	W = 0.2080, ρ_d = 1.0259 gms/cc			
	3	6.47	5.56	29.24
	8	6.43	5.43	30.28
	28	6.55	5.68	29.21
	40	6.47	5.64	28.07
	60	6.47	5.64	28.07
	65	6.47	5.64	28.07
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	3	5.58	5.03	20.04
	10	5.62	4.96	21.45
	25	5.54	5.03	19.46
	45	5.60	5.00	18.44
	140	5.54	5.03	19.46
	300	5.54	5.03	19.46
	480	5.50	5.04	18.85

TABLE V (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 gms/cc			
	3	5.21	4.70	17.88
	7	5.21	4.88	16.02
	10	5.25	4.88	16.62
	15	5.25	4.84	17.06
	20	5.25	4.88	16.62
	30	5.30	4.88	17.43
	60	5.30	4.96	16.62
	120	5.29	5.04	15.71
	300	5.37	5.21	15.32
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	3	5.21	5.04	14.65
	5	5.21	4.89	16.04
	10	5.12	4.87	14.86
Run 7	W = 0.3676, ρ_d = 1.0409			
	3	4.79	4.79	11.29
	6	4.84	4.71	12.55
	8	4.92	4.92	11.91
	10	4.75	4.71	13.95
	15	4.92	4.92	11.91
	20	4.79	4.71	11.92
	30	4.79	4.71	11.92
	60	4.88	4.79	12.41
	300	4.96	4.88	12.74

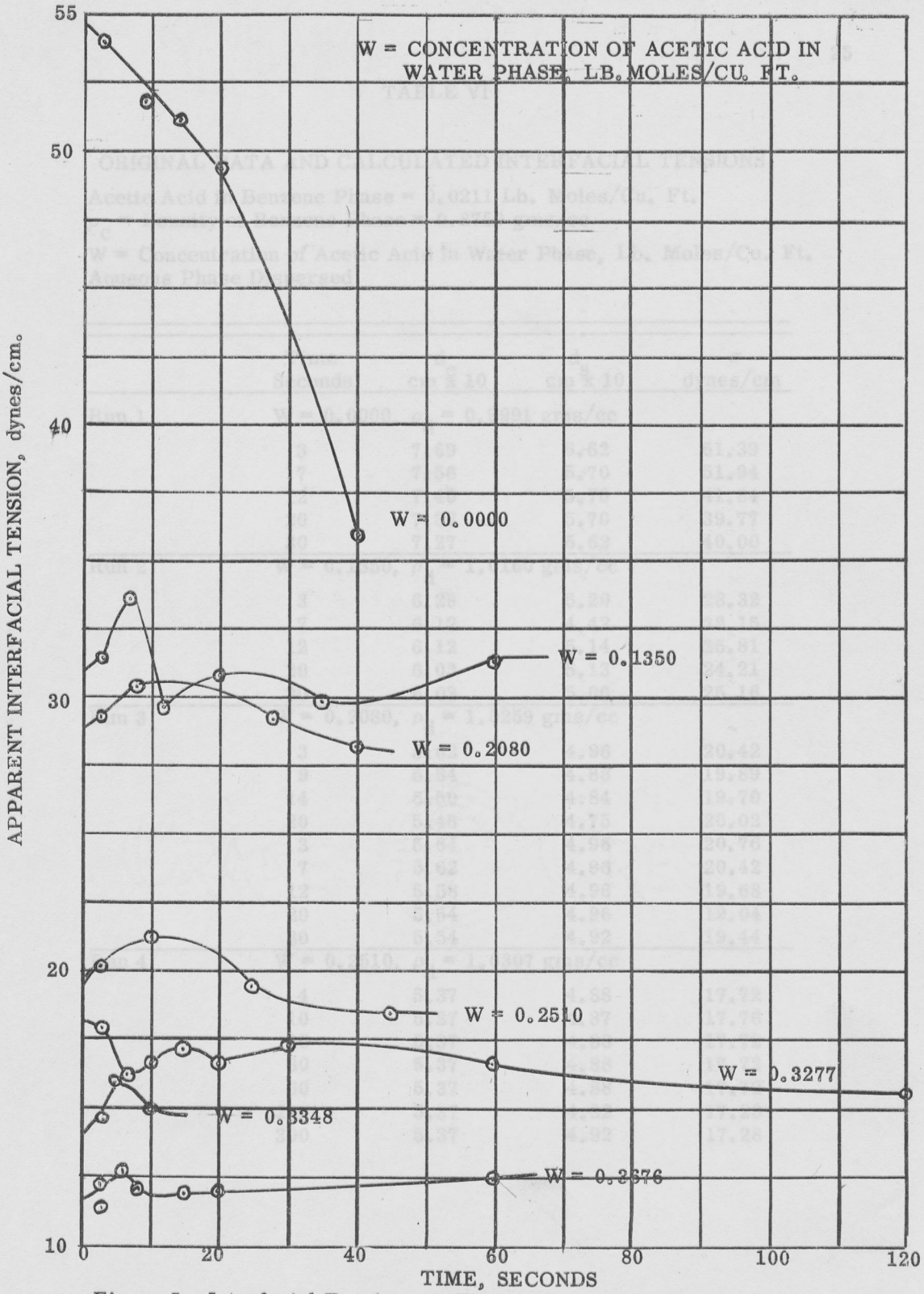

Figure 5. Interfacial Tension vs. Time in Benzene-Acetic Acid-Water System. Acid Concentration in Benzene Phase = 0.0153 Lb. Moles/Cu. Ft.

TABLE VI

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0211 Lb. Moles/Cu. Ft.
ρ_c = Density of Benzene Phase = 0.8759 gms/cc
W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft.
Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	3	7.69	5.62	51.39
	7	7.56	5.70	51.94
	12	7.40	5.70	41.84
	20	7.32	5.70	39.77
	30	7.27	5.62	40.00
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	3	6.28	5.20	28.32
	7	6.12	4.42	38.15
	12	6.12	5.14	25.81
	20	6.03	5.13	24.21
	30	6.03	5.06	25.16
Run 3	W = 0.2080, ρ_d = 1.0259 gms/cc			
	3	5.62	4.96	20.42
	9	5.54	4.88	19.89
	14	5.50	4.84	19.70
	20	5.46	4.75	20.02
	3	5.64	4.96	20.76
	7	5.62	4.96	20.42
	12	5.58	4.96	19.68
	20	5.54	4.96	19.04
	30	5.54	4.92	19.44
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	4	5.37	4.88	17.72
	10	5.37	4.87	17.76
	20	5.37	4.88	17.72
	30	5.37	4.88	17.72
	60	5.37	4.88	17.72
	210	5.37	4.92	17.28
	300	5.37	4.92	17.28

TABLE VI (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 gms/cc			
	4	5.08	4.79	14.76
	8	5.08	4.79	14.76
	12	5.00	4.71	14.34
	16	4.96	4.63	14.54
	30	4.96	4.55	14.28
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	3	5.12	4.89	14.63
	7	5.08	4.88	14.29
	12	5.08	4.84	14.67
	20	5.05	4.88	14.08
	30	5.05	4.89	13.96
	60	5.05	4.88	14.08
Run 7	W = 0.3676, ρ_d = 1.0409 gms/cc			
	3	4.79	4.67	13.57
	9	4.75	4.59	12.33
	14	4.75	4.63	11.96
	20	4.75	4.62	12.04
	30	4.75	4.64	11.89
	60	4.79	4.56	13.09
	120	4.79	4.61	12.68

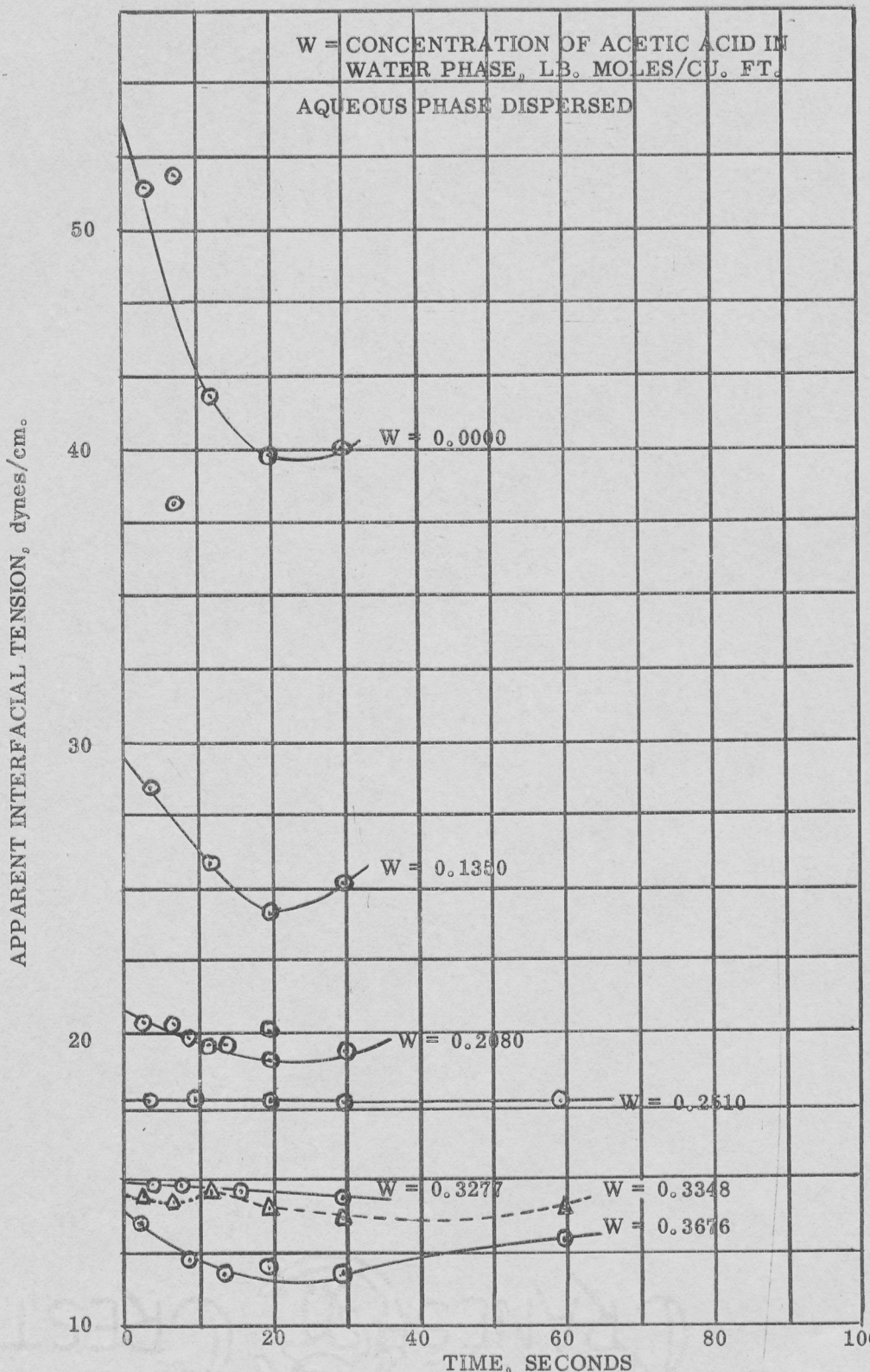

Figure 6. Interfacial Tension vs. Time for Benzene-Acetic Acid-Water System. Acetic Acid Concentration in Benzene Phase Constant = 0.0211 Lb. Moles/Cu.Ft.

TABLE VII

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0332 Lb. Moles/Cu. Ft.
ρ_c = Density of Benzene Phase = 0.8772 gms/cc

W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft.
Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	3	7.40	5.62	42.99
	7	7.27	5.62	39.60
	2	7.40	5.70	41.42
	6	7.32	5.70	39.38
	9	7.44	5.54	45.50
	14	7.27	5.62	39.60
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	5	6.24	5.10	28.70
	4	6.24	5.19	27.33
	9	6.13	5.19	25.10
	12	6.09	5.17	24.61
	15	6.13	4.99	28.01
	2	6.06	5.19	23.82
	6	6.20	5.19	26.50
	10	6.13	5.11	26.32
	20	6.05	5.10	24.79
	40	5.87	5.84	14.43
Run 3	W = 0.2080, ρ_d = 1.0259 gms /cc			
	5	5.69	4.97	21.32
	8	5.69	4.96	21.41
	12	5.63	4.96	20.37
	15	5.62	4.96	21.24
	22	5.65	4.96	20.63
	40	5.62	4.70	23.42
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	3	5.26	4.77	16.90
	7	5.22	4.85	15.53
	12	5.18	4.85	14.97
	20	5.22	4.81	15.94
	30	5.34	4.85	17.37
	60	5.30	4.88	11.87
	120	5.11	4.85	13.98
	300	5.10	4.81	14.20

TABLE VII (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 gms/cc			
	3	4.79	4.45	13.70
	5	4.74	4.51	12.54
	16	4.73	4.43	13.08
	20	4.66	4.51	11.81
	40	4.70	4.55	11.66
	90	4.70	4.58	14.52
	200	4.75	4.66	11.44
	300	4.81	4.73	11.67
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	2	4.85	4.66	12.77
	3	4.66	4.39	12.51
	4	4.81	4.73	11.72
	5	4.81	4.55	13.15
	10	4.73	4.51	12.46
	20	4.66	4.43	12.17
	40	4.77	4.58	15.11
	100	4.77	4.58	15.11
Run 7	W = 0.3676, ρ_d = 1.0409 gms/cc			
	2	4.81	4.66	12.39
	7	4.81	4.58	13.10
	12	4.77	4.55	12.81
	20	4.82	4.69	12.33
	30	4.82	4.69	12.33

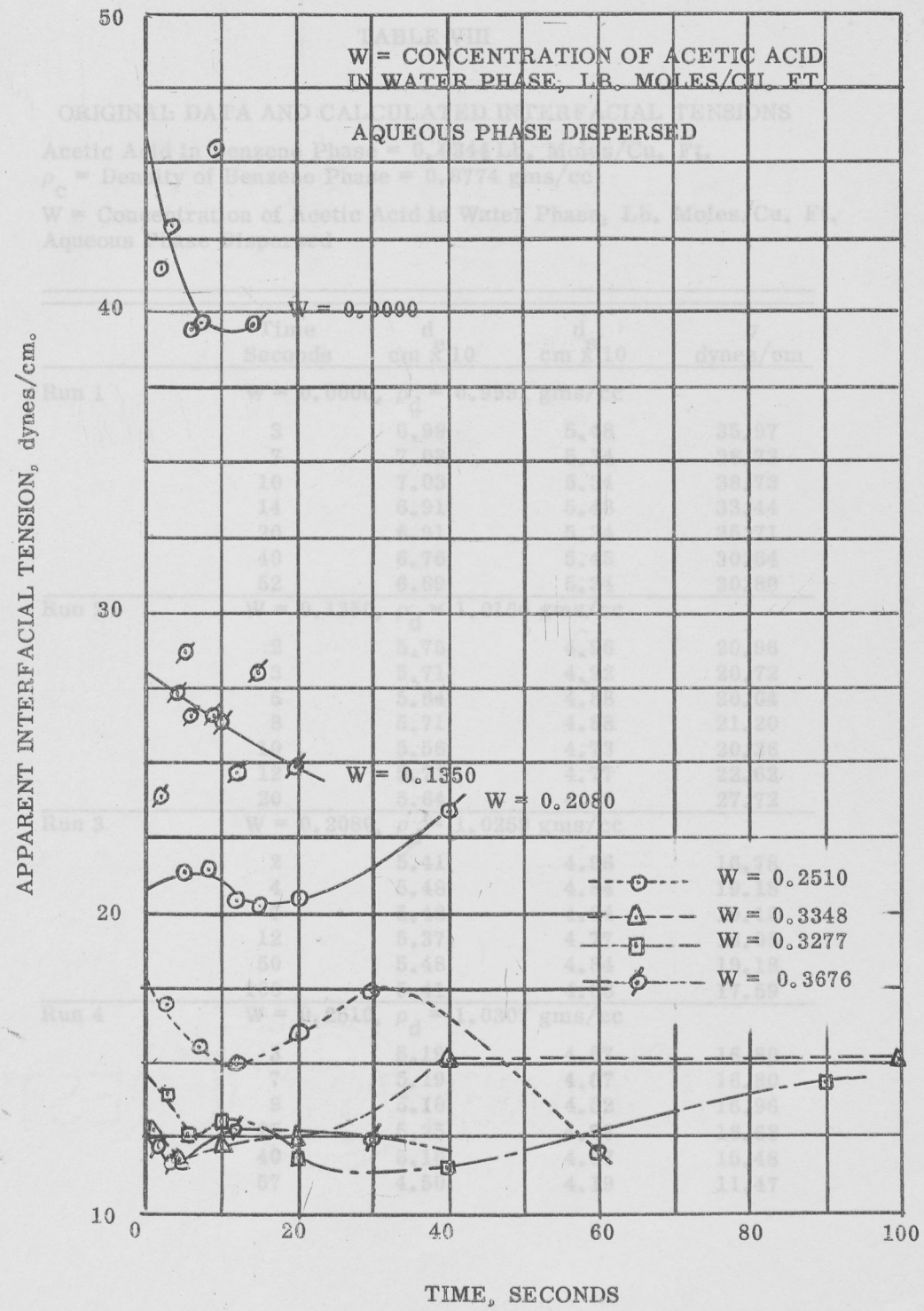

Figure 7. Interfacial Tension vs. Time for Benzene-Acetic Acid-Water System. Concentration of Acetic Acid in Benzene Phase Constant = 0.0332 Lb. Moles/Cu. Ft.

TABLE VIII

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0344 Lb. Moles/Cu. Ft.
ρ_c = Density of Benzene Phase = 0.8774 gms/cc
W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft.
Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	3	6.99	5.48	35.97
	7	7.03	5.34	38.73
	10	7.03	5.34	38.73
	14	6.91	5.48	33.44
	20	6.91	5.34	35.71
	40	6.76	5.45	30.64
	52	6.69	5.34	30.80
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	2	5.75	4.96	20.96
	3	5.71	4.92	20.72
	5	5.64	4.88	20.04
	8	5.71	4.88	21.20
	10	5.56	4.73	20.36
	12	5.71	4.77	22.62
	20	5.64	4.66	27.72
Run 3	W = 0.2080, ρ_d = 1.0259 gms/cc			
	2	5.41	4.96	16.78
	4	5.48	4.84	19.18
	7	5.48	4.84	19.18
	12	5.37	4.77	18.08
	50	5.48	4.84	19.18
	100	5.41	4.88	17.59
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	3	5.19	4.67	16.80
	7	5.19	4.67	16.80
	9	5.10	4.52	16.96
	25	5.25	4.78	16.68
	40	5.10	4.67	15.48
	57	4.50	4.19	11.47

TABLE VIII (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 gms/cc			
	2	4.96	4.81	12.89
	5	4.96	4.73	13.59
	10	4.96	4.66	14.17
	15	4.92	4.66	13.64
	30	4.96	4.66	14.17
	50	4.96	4.66	14.17
	100	4.88	4.51	14.42
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	2	4.81	4.43	14.22
	8	4.73	4.43	13.11
	20	4.73	4.43	13.11
Run 7	W = 0.3676, ρ_d = 1.0409 gms/cc			
	5	5.11	5.04	13.26
	6	4.96	4.85	12.81
	10	5.04	4.96	12.98
	12	4.90	4.81	12.34
	17	5.11	5.04	13.26
	30	5.11	5.11	12.67
	40	4.96	4.92	12.26

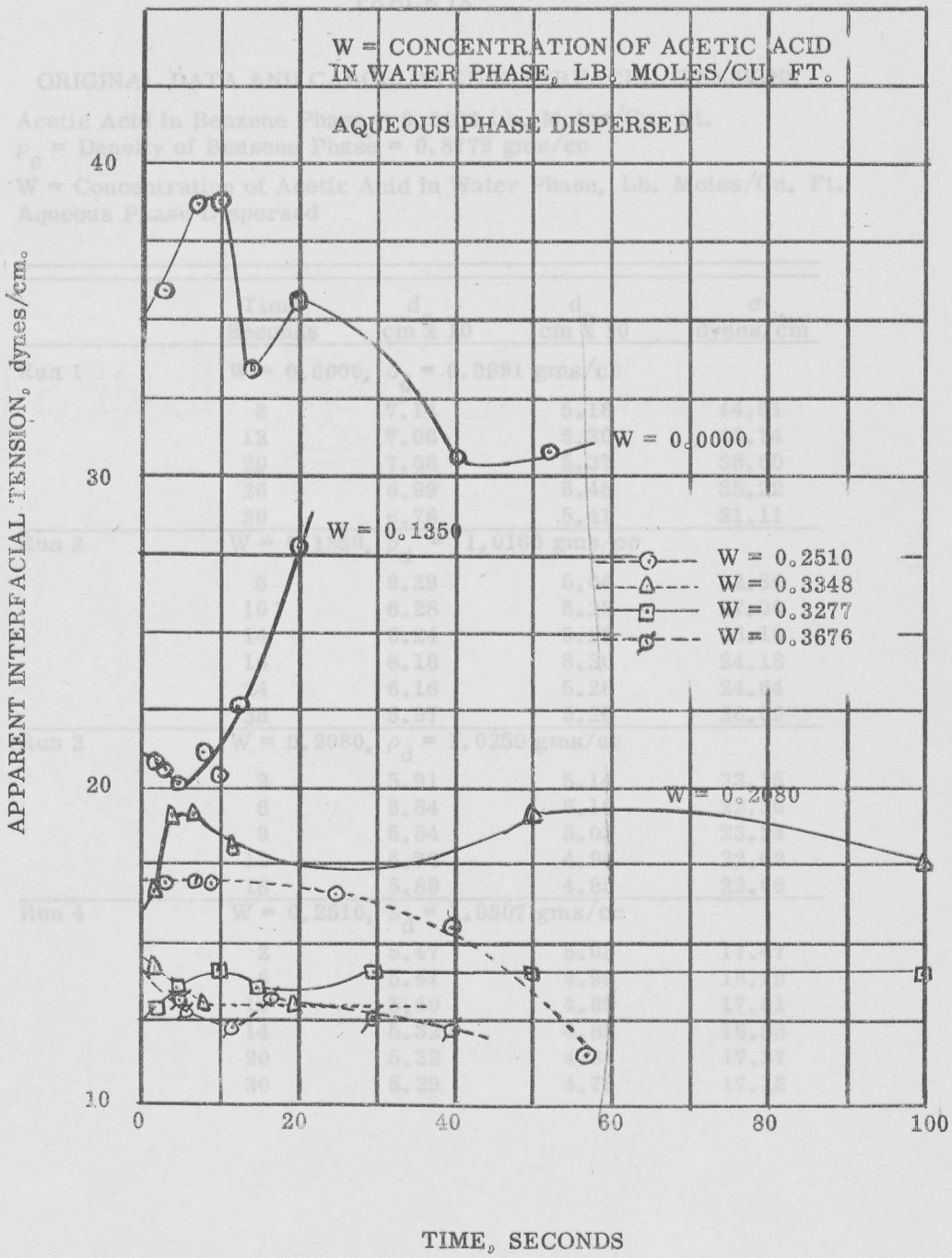

Figure 8. Interfacial Tension vs. Time for Benzene-Acetic Acid-Water. Concentration of Acetic Acid in Benzene Phase Constant = 0.0332 Lb. Moles/Cu. Ft.

TABLE IX

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Acetic Acid in Benzene Phase = 0.0403 Lb. Moles/Cu. Ft.
ρ_c = Density of Benzene Phase = 0.8779 gms/cc
W = Concentration of Acetic Acid in Water Phase, Lb. Moles/Cu. Ft.
Aqueous Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	W = 0.0000, ρ_d = 0.9991 gms/cc			
	8	7.14	5.18	44.51
	12	7.06	5.26	40.74
	20	7.06	5.37	38.60
	26	6.99	5.45	35.22
	30	6.76	5.41	31.11
Run 2	W = 0.1350, ρ_d = 1.0160 gms/cc			
	5	6.39	5.04	32.86
	10	6.28	5.26	27.00
	14	6.24	5.26	26.10
	16	6.16	5.30	24.18
	24	6.16	5.26	24.64
	35	5.97	5.26	26.09
Run 3	W = 0.2080, ρ_d = 1.0259 gms/cc			
	2	5.91	5.14	23.15
	6	5.84	5.10	22.36
	9	5.84	5.03	23.24
	12	5.76	4.96	22.62
	16	5.69	4.85	22.68
Run 4	W = 0.2510, ρ_d = 1.0307 gms/cc			
	2	5.47	5.03	17.47
	6	5.47	4.96	18.19
	10	5.40	4.89	17.81
	14	5.32	4.85	16.95
	20	5.32	4.81	17.37
	30	5.29	4.78	17.18

TABLE IX (Continued)

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 5	W = 0.3277, ρ_d = 1.0380 gms/cc			
	2	5.03	4.67	15.12
	7	5.03	4.78	14.09
	12	5.07	4.81	14.35
	18	5.03	4.67	15.12
	26	4.96	4.60	14.74
Run 6	W = 0.3348, ρ_d = 1.0387 gms/cc			
	5	5.04	5.06	12.62
	10	5.09	4.96	13.43
	14	5.16	5.03	12.96
	19	5.09	5.06	12.62
	30	5.16	5.03	12.90
	50	4.99	4.89	12.68
	100	4.96	4.69	13.92
Run 7	W = 0.3676, ρ_d = 1.0409 gms/cc			
	3	5.13	4.76	16.02
	5	5.09	4.79	15.11
	10	5.13	4.83	15.35
	20	5.13	4.76	16.02
	30	5.16	4.88	15.27

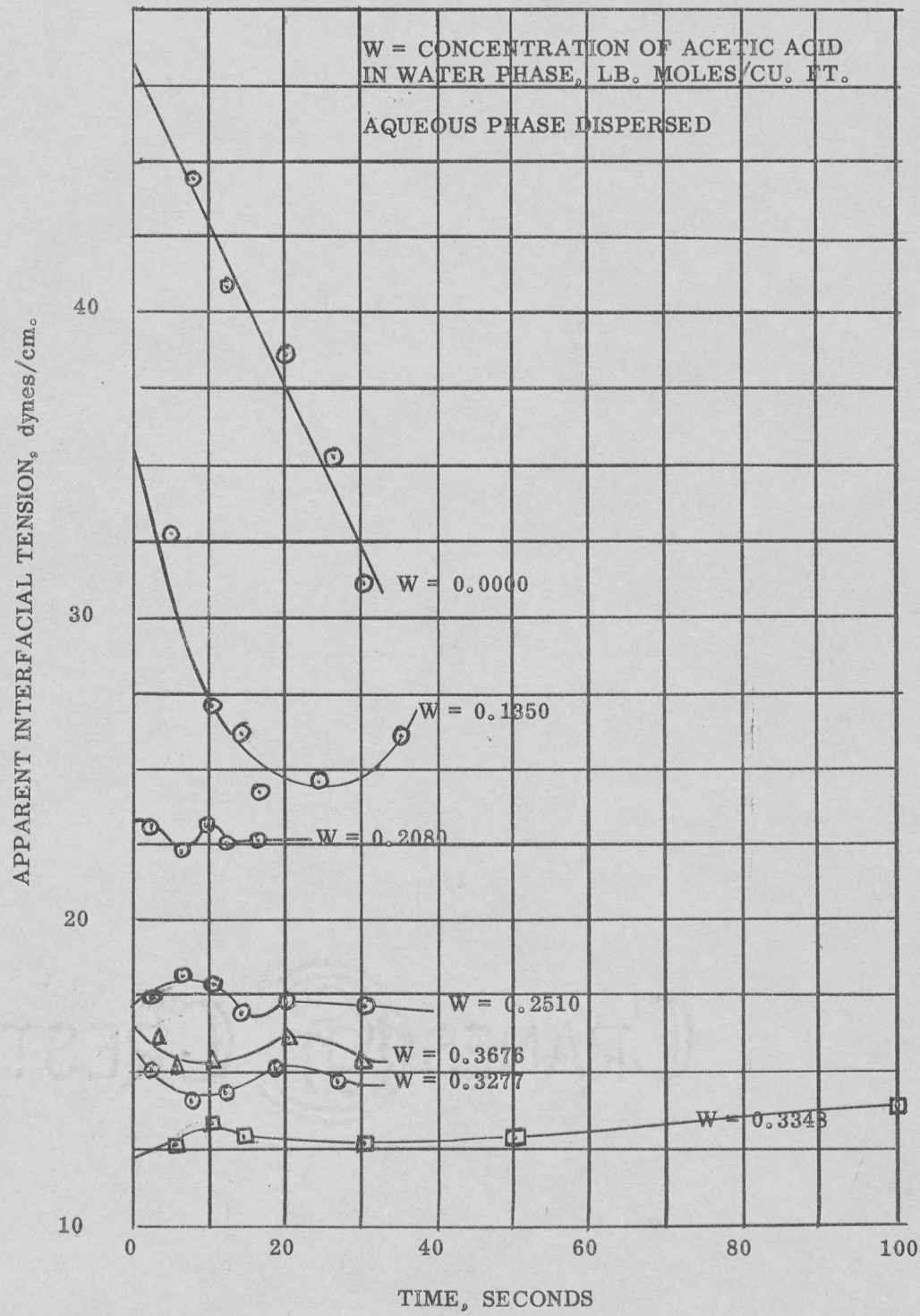

Figure 9. Interfacial Tension vs. Time for Benzene -Acetic Acid - Water System Concentration of Acetic Acid in Benzene Phase Constant = 0.0403 Lb. Moles/Cu. Ft.

TABLE X

ORIGINAL DATA AND CALCULATED INTERFACIAL TENSIONS

Benzene-Acetic Acid-Water System
Measurements With Inverted Tip
C = Acetic Acid Concentration in Benzene Phase , Lb. Moles/Cu. Ft.
Density = ρ_c gms/cc

W = Acetic Acid Concentration in Water Phase, Density = ρ_d gms/cc

Benzene Phase Dispersed

	Time Seconds	d_e cm x 10	d_s cm x 10	σ dynes/cm
Run 1	C = 0.0403, W = 0.2080, ρ_d = 1.0259, ρ_c = 0.8779			
	2	5.24	4.84	15.33
	6	5.15	4.86	13.92
	10	5.20	4.84	14.78
	21	5.15	4.84	14.07
	35	5.10	4.82	13.61
	50	5.15	4.82	14.26
	100	5.17	4.91	13.76
Run 2	C = 0.0403, W = 0.3348, ρ_d = 1.0387, ρ_c = 0.8779			
	3	4.77	4.72	11.22
	10	4.77	4.77	10.86
	15	4.77	4.67	11.61
	25	4.77	4.67	11.61
	50	4.67	4.62	10.79
	100	4.62	4.48	11.20
Run 3	C = 0.0200, W = 0.3676, ρ_d = 1.0409, ρ_c = 0.8759			
	2	4.44	4.31	10.58
	2	4.62	4.58	10.77
	8	4.62	4.58	10.77
	14	4.62	4.48	11.49
	25	4.62	4.53	11.15
	50	4.62	4.53	11.15
	100	4.62	4.53	11.15
Run 4	C = 0.0211, W = 0.1350, ρ_d = 1.0160, ρ_c = 0.8759			
	3	5.77	5.20	18.92
	6	5.72	5.17	18.42
	2	5.71	5.15	18.48
	10	5.72	5.17	18.42
	20	5.72	5.15	18.64
	50	5.71	5.17	18.31
	100	5.72	5.17	18.55

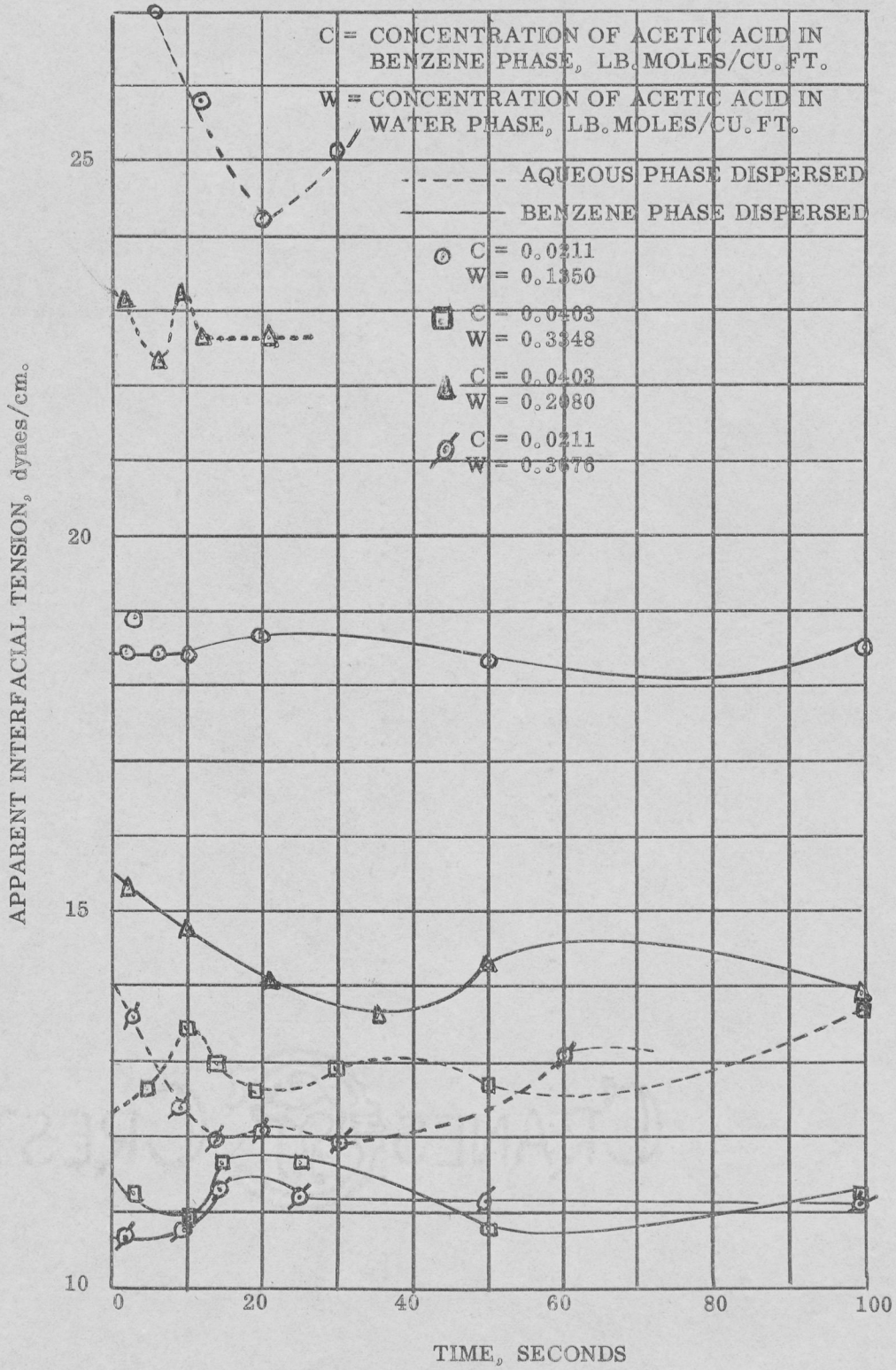

Figure 10. Comparison of Interfacial Tension With Benzene Phase Dispersed and Aqueous Phase Dispersed.

TABLE XI

APPARENT INTERFACIAL TENSION

BENZENE-ACETIC ACID-WATER SYSTEM 77°F

Acid Concentration in Water Phase Lb. Moles/Cu. Ft.	Acid Concentration in Water Phase Lb. Moles/Cu. Ft.						
	0.0000	0.0069	0.0153	0.0211	0.0332	0.0344	0.0403
0.0000	42.80	54.50	54.50	53.00	45.50	35.00	48.25
0.1350	23.00	28.50	31.00	29.25	28.00	21.00	30.05
0.2080	12.50	22.00	28.90	20.75	20.75	16.25	23.25
0.2510	13.00	19.50	19.80	17.75	17.75	16.75	17.00
0.3277	12.00	14.50	18.00	15.00	14.50	12.50	15.25
0.3348	11.25	16.00	14.00	14.50	13.00	14.75	12.25
0.3676	13.00	17.50	11.25	14.00	11.75	14.00	16.50

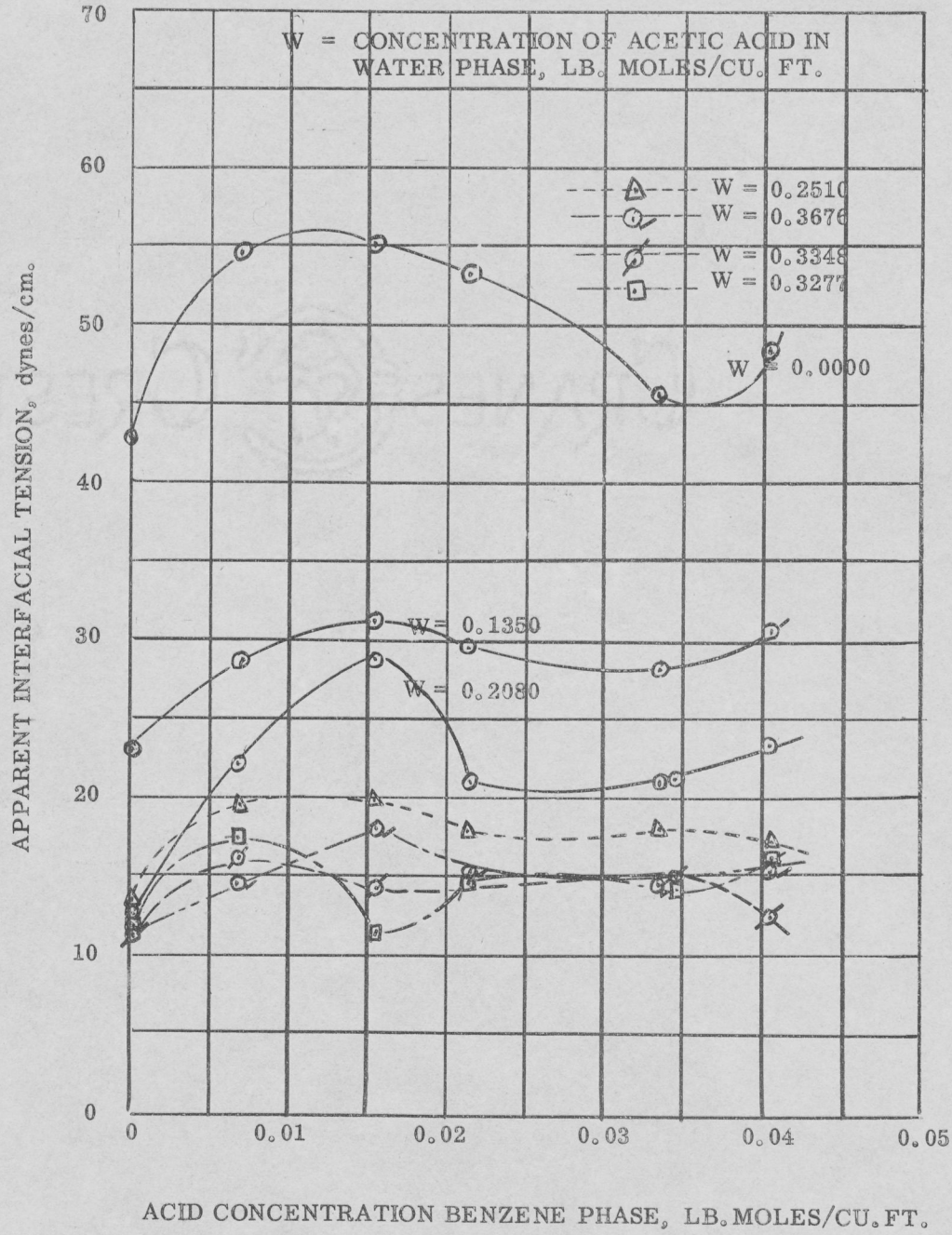

Figure 11. Apparent Interfacial Tension vs. Acid Concentration in the Benzene Phase at Interface.

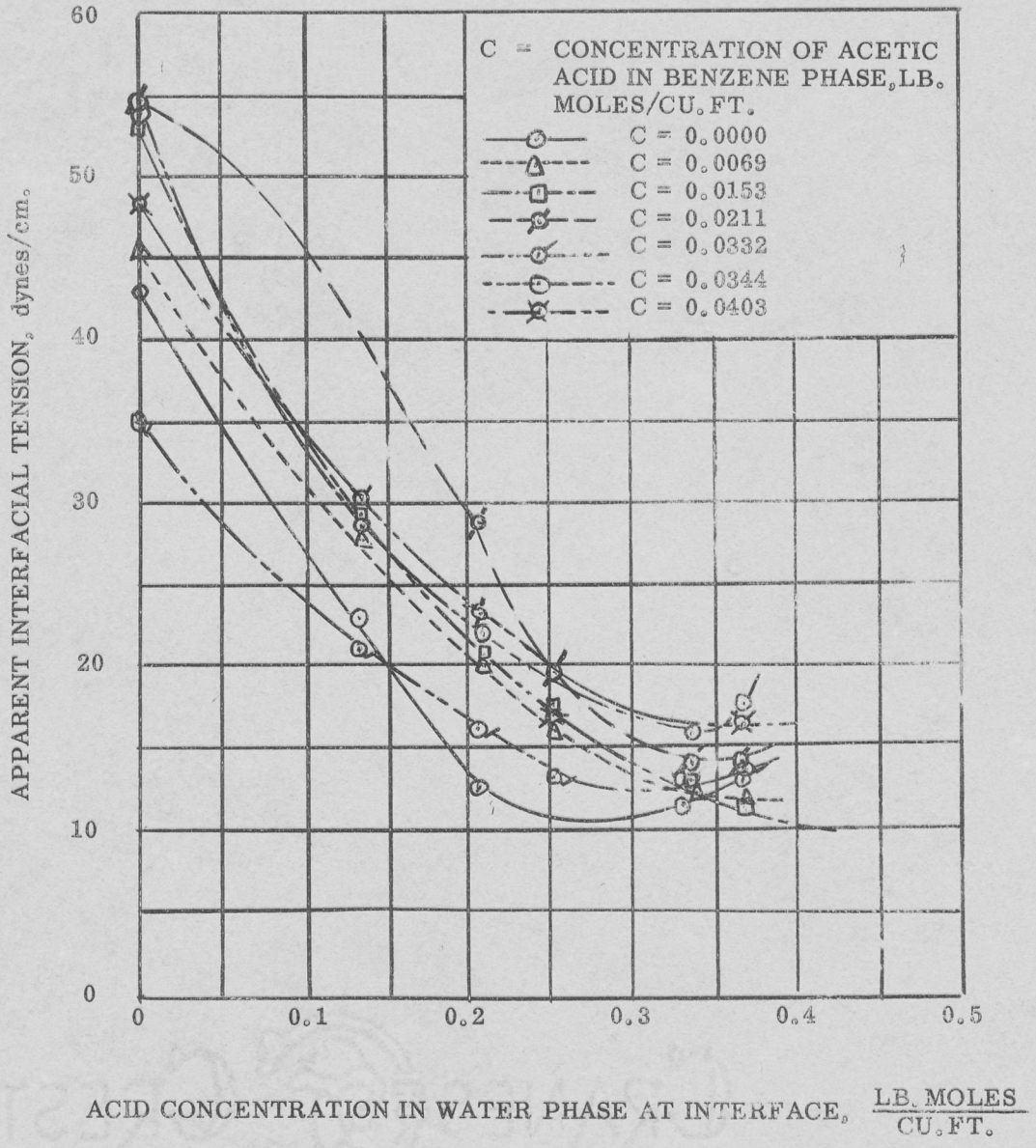

Figure 12. Apparent Interfacial Tension vs. Acid Concentration in the Water Phase at Interface.

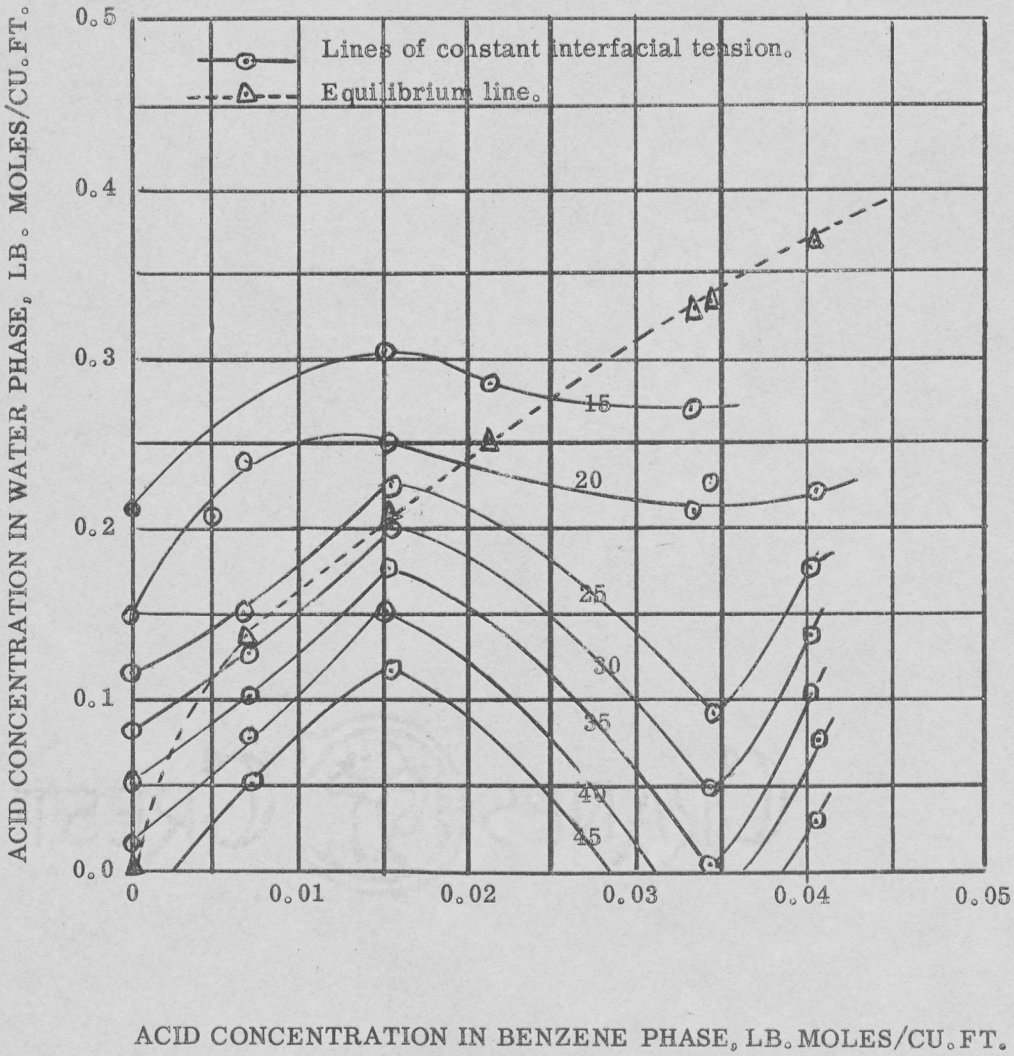

Figure 13. Interfacial Tension in the Benzene-Acetic Acid-Water System. 77°F.

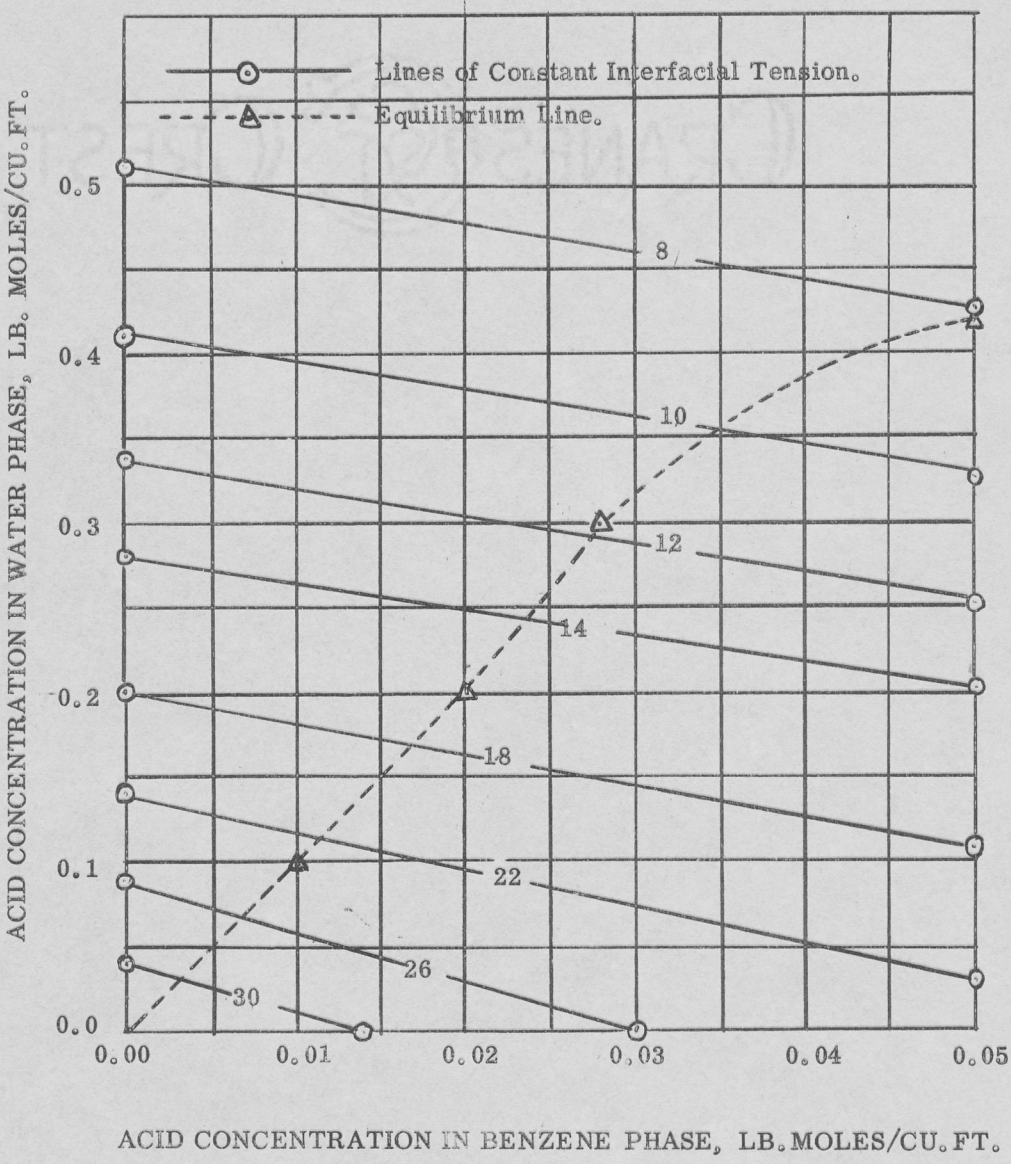

Figure 14. Interfacial Tension in the Benzene-Acetic Acid-Water System From Collins[2].

DISCUSSION OF RESULTS

The results obtained do not appear to be conclusive although several interesting things appear in their correlation. For Fig. 3 to 9 where interfacial tension is plotted as a function of time for 49 different combinations of the benzene-acetic acid-water system, a definite wave characteristic is apparent. This may be due to characteristic changes in the drop dimensions due to momentum. The effect was more pronounced when the concentration differences were greater so the wave may be caused by surface effects set up by mass transfer.

There were a number of sources of error present. One came about due to the use of flood lights to illuminate the drops. This gave rise to an increase in temperature. To hold this error to a minimum, the floodlights were used only when necessary. Another, and probably more serious error came about due to measurement. The method used requires considerable precision. An error of 0.05 mm in d_e gave rise to about 2.5 per cent error in surface tension. This was increased to 10 per cent for a 0.10 mm error. It is believed that this error for the determinations reported was in the range of $\pm$ 0.05 mm. The effect of mass transfer on the higher concentration differences often made the outline of the drop difficult to determine as may be seen in Fig. 15.

The value of interfacial tension for an equilibrium mixture of benzene and water (no acetic acid) was 40.89 dynes/cm. This compares to an actual value of 35.0 dynes/cm.[1] This error may be due in part to impurities present in the benzene or in the water. Extremely pure benzene is difficult to obtain.

The results obtained in the measurements of interfacial tension

were reproduceable. Several checking results were obtained for each of the seven equilibrium mixtures. Table VI, Run 3 gives an indication of the reproducibility of non-equilibrium mixtures. Two frames taken at three seconds (same concentration) gave 20.42 and 20.76 dynes/cm. for the interfacial tension which is a variation of 1.64 per cent. In the same run, two values for interfacial tension obtained at 20 seconds gave 19.04 and 20.02 dynes/cm. which is a variation of 4.85 per cent. Table X, Run 3 gives some indication of the reproducibility of the inverted tip results.

The results obtained by this method do not check very well with those obtained by Collins.[2] (See Fig. 14). In general the results are higher. For example, Collins obtained for 0.6669 lb moles/cu. ft., in the benzene phase, interfacial tensions on the order of 1.5 dynes/cm. The lowest values obtained using the pendant drop method were on the order of 11.0 dynes/cm. The highest values obtained by Collins were around 30.0 dynes/cm. whereas using the pendant drop method values as high as 54.5 dynes/cm. were obtained. These high values for interfacial tension occured for the case of transfer of acetic acid to the water phase from the benzene phase when the water phase had 0 concentration of acetic acid. In general, the equilibrium mixtures for each of the seven series gave horizontal lines and again the values were greater than those determined by Collins.

The results obtained by using an inverted tip (benzene phase dispersed) were in all cases lower than the results in which the aqueous phase was dispersed. (See Fig. 10 for comparison of the two methods.) This is probably due to some unknown surface effect, since theoretically the drop position should have no bearing on the results.

There are factors which may hinder future work of using the pen-

dant drop method for determining interfacial tensions in non-equilibrium systems. One of these is the fact previously mentioned of surface effects of mass transfer which make the boundary indistinct. (See Fig. 15.) Another is the fact that diffusion may take place up into or out of the liquid column above the drop depending on the concentrations of acid in the two phases. The equations derived for surface tension were based on a static system and any effects which tend to make the system otherwise introduce complications. The method has the advantage of ease of operation and speed with which initial readings may be obtained. This is a tremendous advantage since the final outcome of the investigation depends on the extrapolation of interfacial tension to zero time.

CRANE'S CREST

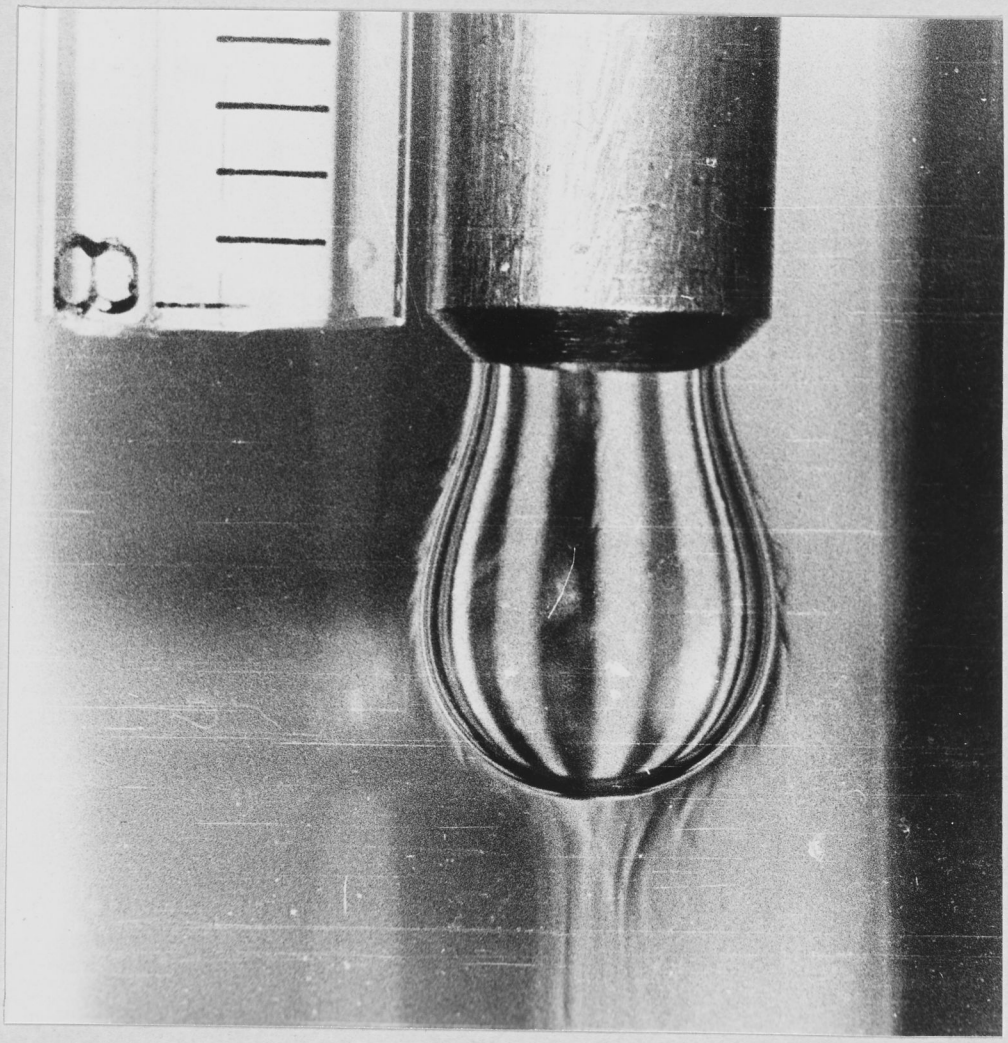

Figure 15. Actual photograph of drop in which the effects of mass transfer are visible.

CONCLUSIONS AND RECOMMENDATIONS

Since the results do not check with Collins, it is suggested that another attempt be made using a modified procedure. The results appear to be somewhat erratic.

One method which might prove useful would be to obtain a continuous record of the drop from time of formation by use of motion picture studies. Further refinements in apparatus such as the use of optically flat glass throughout the system would also aid in obtaining conclusive results.

CRANES CREST

NOMENCLATURE

β = a parameter of the dimensionless form of the differential describing a static drop which is defined as $\beta = \frac{g}{g_c} \frac{(\rho_d - \rho_c)\, b^2}{\sigma}$

b = radius of curvature of the drop at origin with the origin being chosen as the bottom of the drop.

C = concentration of acetic acid in the benzene phase, lb. moles/cu. ft.

d_e = diameter of drop at equator.

d_s = diameter of drop at the selected plane.

g = acceleration of gravity.

g_c = conversion factor.

H = a function of the ratio of the diameter at the equator to the diameter at the selected plane defined by H.

Δp = pressure differential between dispersed and continuous phases.

ρ_c = density of continuous phase.

ρ_d = density of dispersed phase.

r_1 & r_2 = principal radii of curvature.

S = the ratio of the diameter of the drop at the selected plane to the diameter at the equator.

t = time, seconds.

W = concentration of acetic acid in the aqueous phase, lb. moles/cu. ft.

x = horizontal distance from center of nozzle.

X = the ratio of the horizontal distance from the center of the nozzle to the radius of curvature at the origin.

z = vertical coordinate with origin taken at bottom of drop.

Z = the ratio of the vertical coordinate to the radius of curvature the origin.

Z′ = the first derivative of Z with respect to X.

Z″ = the second derivative of Z with respect to X.

BIBLIOGRAPHY

1. Andreas, J. M., E. A. Hauser, and W. B. Tucker, "Boundary Tensions by Pendant Drops", J. Phys. Chem., 42, 1001, (1938).

2. Collins, Robert L., "Interfacial Tension by the Ring Method in Non-Equilibrium Liquid-Liquid Systems", Univ. of Tennessee B. S. Thesis, (June 1950).

3. Hodgman, Charles D., Handbook of Chemistry and Physics - 34 ed., 1869, Chem. Rubber Publishing Co., Cleveland, Ohio, (1952).

4. Sigwarf, K., and Nassenstein, H., "Reaction at the Interface of Two Liquid Phases", Die Naturwissenscitaflen 42, 458, (1955)

APPENDIX

SAMPLE CALCULATIONS

1) Standardization of sodium hydroxide solutions:

a) Weight of potassium acid phthalate = 6.9994 gms., molecular weight of potassium acid pthalate = 204.2. The sample required 34.90 ml. of NaOH solution.

$$\text{Normality of base} = \frac{6.9994 \times 1000}{204.2 \times 34.90} = 0.9821$$

Two other samples gave 1) 0.9827
2) 0.9845

Average value = 0.9830 gram moles/liter.

This solution was used in titrating the water phase.

b) Weight of potassium acid phthalate = 0.7098 gms. The sample required 35.10 ml. of NaOH solution.

$$\text{Normality of base} = \frac{(0.7098)(1000)}{204.2 \times 35.10} = 0.0990$$

Two other samples gave 1) 0.0990
2) 0.0996

Average value = 0.0992 gram moles/liter.

The benzene solutions were diluted with 100 per cent ethanol and titrated with this solution.

2) Titration of a solution of acetic acid in bezene. (Equilibrium mixture 2.)

A 5 ml. aliquot of benzene-acetic acid mixture required 5.62 ml. of standard base (N = 0.0992). Concentration of acid in benzene phase:

$$\frac{5.62}{5.00} \times 0.0992 \times 28.32 \frac{\text{liters}}{\text{cu. ft.}} \times \frac{1 \text{ lb. mole}}{453.6 \text{ gm. moles}} = 0.0069 \frac{\text{lb. moles}}{\text{cu. ft.}}$$

3) Calculation of apparent interfacial tension.

$$\sigma = \frac{g}{g_c} \times \frac{1}{H} \left(\rho_d - \rho_c\right) d_e^2$$

Where σ = interfacial tension, dynes/cm.

g = acceleration of gravity = 981 cm/sec^2.

g_c = dimensional constant.

$\frac{1}{H}$ = drop characteristic from Table I.

ρ_d = density of disperse phase, gms/cc.

ρ_c = density of continuous phase, gms/cc.

d_e = diameter of the drop at the equator, cm.

For example, take run 1 from Table III, at t = 2 sec.

t = 2 seconds.

d_e = 0.655 cm.

d_s = 0.500 cm.

$S = \frac{d_s}{d_c} = 0.763.$

$\frac{1}{H}$ = 0.648 (From Table I).

ρ_d = 1.0160 gms/cc (From Table II).

ρ_c = 0.8728 gms/cc (From Table II).

$\sigma = 981 \times 0.648 \times (1.0161 - 0.8728)(0.655)^2.$

σ = 39.00 dynes/cm.

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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Date June 2, 1956