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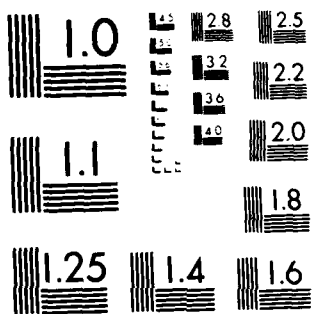   WASHINGTON DC   S E PHIPPEN ET AL. 23 MAY 83 NRL-MR-5098
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

An investigation has been made of the effect of drop rate growth on the interfacial tension as determined by the drop weight method. A series of surfactant concentrations for two different surfactants — Aerosol OT and Witconate P10-59 — yielded data which allowed a corrective equation to be developed.

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CONTENTS

INTERFACIAL TENSION BY THE DROP WEIGHT (VOLUME) METHOD: EFFECT OF DROP GROWTH RATE

I.   INTRODUCTION

The drop volume method is considered to be a very accurate and reproducible technique for the measurement of interfacial tension (IFT) between two liquids providing the following conditions are met:

   a) the orifice is sharply cut and of an accurately known radius

   b) the orifice is carefully ground and fully wetted

   c) the drop is made to detach itself as slowly as possible from the orifice (1,2)

Several improvements have already been made on the method; a correction factor has been developed and refined to increase the precision of the interpretation of the data. Lohnstein (3), and Harkins and Humphrey (4) developed a correction factor, $\psi(r/a)$, to account for the difference between the total volume below the orifice and the actual volume of the falling drop. Harkins and Brown (1) later developed a similar correction factor $f(r/v^{1/3})$ (5), which was easier to obtain. Wilkinson (6) derived a fourth power polynomial equation to mathematically convert the correction factor from $f(r/v^{1/3})$ to $\psi(r/a)$ since the latter is considered more accurate (6).

Improvements have also been made in the delivery technique of the dispersed phase to reduce drop distortion caused by fast flow rates. Wilkinson varied the flow rate of the dispersed phase by hand-turning an Agla micrometer syringe. He formed 95% of the drop rapidly (30 seconds), waited at least 60 seconds, then took 30 seconds to slowly turn off the remaining 5% of the drop (6).

Eva Tornberg (2) constructed a unique apparatus to regulate the flow of the dispersed phase. Tornberg forced the dispersed phase through the syringe with a step motor driven by a variable frequency oscillator. The step motor rotated a screw which depressed a piston causing a drop to form at the orifice of a brass tip. An adjustable oscillator pulse rate (1 to 240 Hz) and interchangeable screws regulated the rate of drop formation. Tornberg formed 90% of the drop at 240 Hz and the last 10% of the drop at 10 Hz to reduce the error produced by fast flow rates in the last stages of drop development (2).

Sharma also developed a new apparatus to deliver the dispersed phase at variable flow rates. The apparatus consists of glass and rubber tubing, stopcocks and Herman's clips with screws. The screws in the rubber tubing were adjusted to control

the flow rate of the dispered phase through a pipette. The flow
rate could be controlled to within $\pm$.006 drops/min. (8).

This investigation was conducted in order to study the
effect of flow rate (uninterrupted) on the error produced in the
calculated interfacial tension value. A correction factor was
derived to calculate the true interfacial tension value from data
obtained at higher constant flow rates. This study concentrates
on low interfacial tension values and moderate flow rates.

II. EXPERIMENTAL PROCEDURE

An Agla Micrometer Syringe Kit, with a metal capillary
needle (r = .0457 cm) attached to the ground nozzle, was used to
determine drop volumes. The volumes were read from a graduated
barrel and these were used to determine the interfacial tension
values. Flow rates were altered by a four watt motor and pulley
system in which a thread was first looped around the micrometer
head and then around the motor-driven pulley (see Figure 1.) Four
volumetric flow rates were investigated:

volumetric flow rates (cm^3/s): 1.33x10^{-4} 2.98x10^{-4} 6.28x10^{-4} 12.8x10^{-4}
pulley diameter (cm):   1.3   3   6   12.5

All measurements were made at 25°C. The two surfactants studied
were Aerosol OT (American Cyanamid) and Witconate P10-59 (Witco
Chemical Co.) Methyl salicylate was used for the dispersed
phase. The concentration of surfactant in the aqueous phase was
varied by diluting the surfactant stock solution with distilled
water. Drops were formed in a five ml beaker filled with four ml
of surfactant solution. At each volumetric flow rate, the volume
of one drop was calculated from the average of ten drops formed
successively. After ten successive drops, the beaker was rinsed
with distilled water and acetone and refilled with surfactant
solution. Again, the volume of one drop was calculated. This
procedure was repeated two to four times at each volumetric flow
rate. The volumes thus obtained were used in the following
equation to calculate an interfacial tension value at each
volumetric flow rate.

$$\gamma = \frac{V\Delta\rho g F}{r} \qquad [1]$$

where: γ = interfacial tension (dynes/cm)

V = volume of one drop (cm^3)

$\Delta\rho$ = density difference between the con-
tinous and dispersed phase (g/cm^3)

F = correction factor =
0.14782 + 0.27896(r/v$^{1/3}$) - 0.166(r/v$^{1/3}$)^2

g = gravitation constant

r = capillary radius (cm)

III. <u>RESULTS AND DISCUSSION</u>

To determine the effect of flow rate upon the calculated interfacial tension, graphs were made of interfacial tension vs. volumetric flow rate at selected surfactant concentrations (see Figures 2 and 3). The calculated interfacial tension was found to be a linear function of flow rate at high surfactant concentration and low interfacial tension values. As the interfacial tension increased with decreasing surfactant concentration, the relationship became increasingly curvilinear. An empirical equation was developed to establish a relationship between the calculated interfacial tension and flow rate:

$$\text{or} \qquad \gamma_v = b \sqrt{v} + \gamma_0 \qquad\qquad [2]$$

where: γ_v = calculated interfacial tension (dynes/cm) at the corresponding flow rate

γ_0 = true interfacial tension (dynes/cm) at an infinitely slow rate (v = 0)

b = slope of relation

v = volumetric flow rate (cm³/s)

Figures 2 and 3 illustrate the experimental data obtained.

A least squares plot was made to determine the constant b and true interfacial tension for each surfactant dilution over the range of flow rates allowed by the experimental equipment. The results of this exercise for each surfactant are reported in Tables 1 and 2. The ratios of true (extrapolated) interfacial tension to the b parameter, γ_0/b, were analyzed statistically. It was found that over the range of interfacial tension studied the mean value of γ_0/b was 0.1178 with a standard deviation of 0.0214 and is applicable to both surfactants.

Equation [2] may therefore be rearranged into the form:

$$\frac{\gamma_v - \gamma_0}{\gamma_0} = \frac{b}{\gamma_0} \sqrt{v} \qquad\qquad [3]$$

after dividing through by γ_0. Since the existing data suggest that γ_0/b = constant, equation [3] may be rearranged to:

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$$\gamma_0 = \left(\frac{b'}{b' + \sqrt{v}}\right) \gamma_v \qquad [4]$$

where $b' = \gamma_0/b = 0.1178$

or

$$\gamma_0 = k_v \gamma_v \qquad [5]$$

where $k_v = \left(\frac{0.1178}{0.1178 + \sqrt{v}}\right) =$ correction factor

Using the present drop volume apparatus, an excellent estimate may be made of the true IFT when equation [5] is used to determine the corrective factor k_v. Table 3 illustrates values of γ_0 extrapolated at $v = 0$ and values of γ_0 calculated using equation [5].

The data collected here, however, are for two surfactants. It is not known how surfactants which may be predisposed to producing strong surface tension aging effects may impact upon the results presented here. However, it is felt that this analysis suggests a meaningful method by which drop formation rates may be accounted for in the determination or estimation of the true interfacial tension.

IV. RECOMMENDED FUTURE PROJECTS

1. This study was conducted using two anionic surfactants: Aerosol OT and Witconate P10-59. It would be useful to repeat the above procedure and calculations for nonionic and cationic surfactants to determine the extent that the corrective procedures presented here for two surfactants applies in the general case.

2. It would be worthwhile to determine what kind of complications develop when a corrective procedure such as this is used in the case of surfactants which produce strong surface aging effects.

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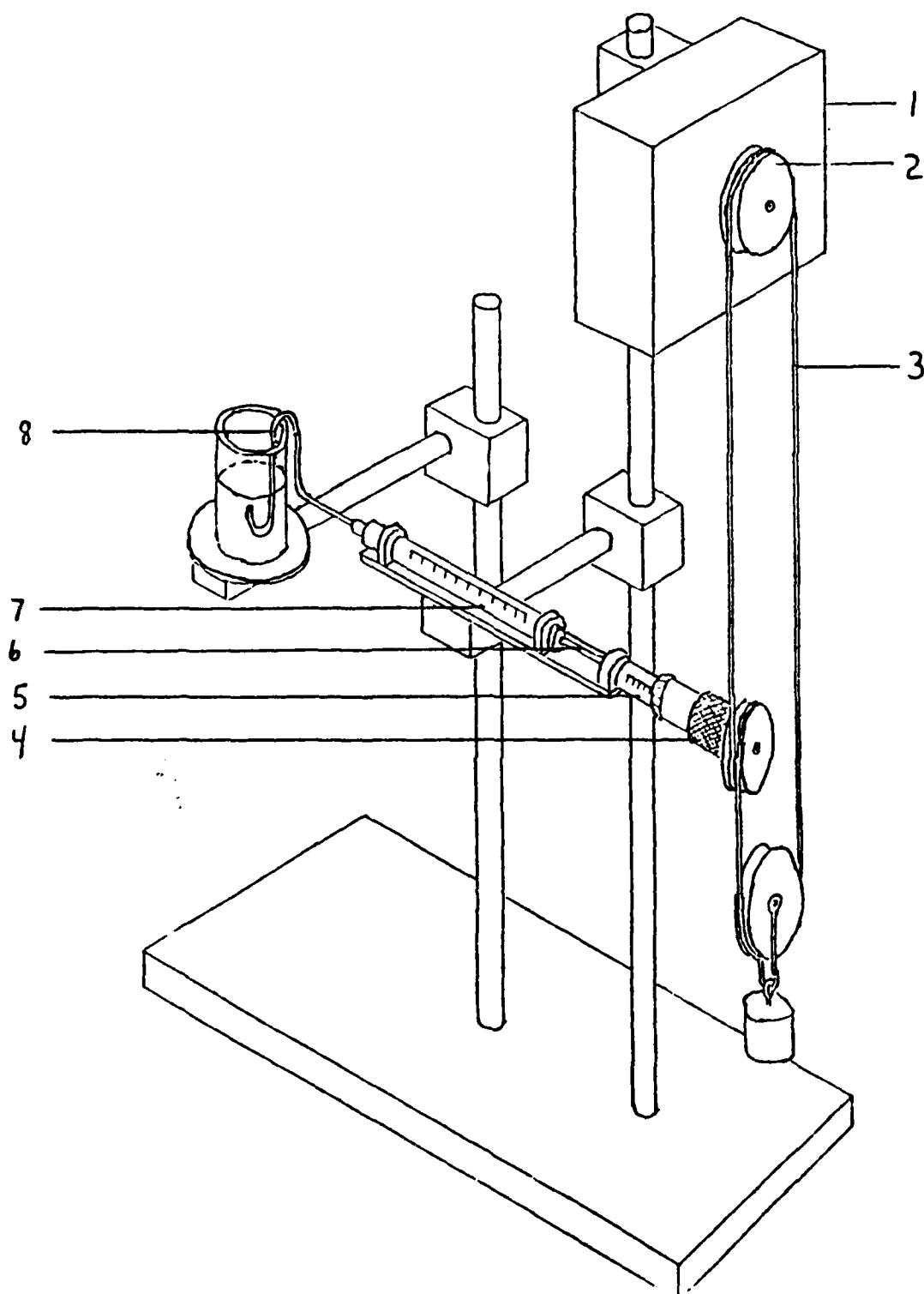
Figure 1. Diagram of Agla-Micrometer Syringe: 1) 4 watt motor;
2) pulley; 3) thread; 4) micrometer head; 5) graduated
barrel 6) metal plunger; 7) glass syringe; 8) metal
capillary needle

Figure 2. Plot of Calculated Interfacial Tension vs. Square Root of Volumetric Flow Rate for Aerosol OT Solutions: 1) .70 wt. percent; 2) .27 wt. percent; 3) .24 wt. percent; 4) .1 wt. percent; 5) .063 wt. percent; 6) .053 wt. percent; 7) .047 wt. percent; 8) .037 wt. percent; 9) .021 wt. percent; 10) .007 wt. percent

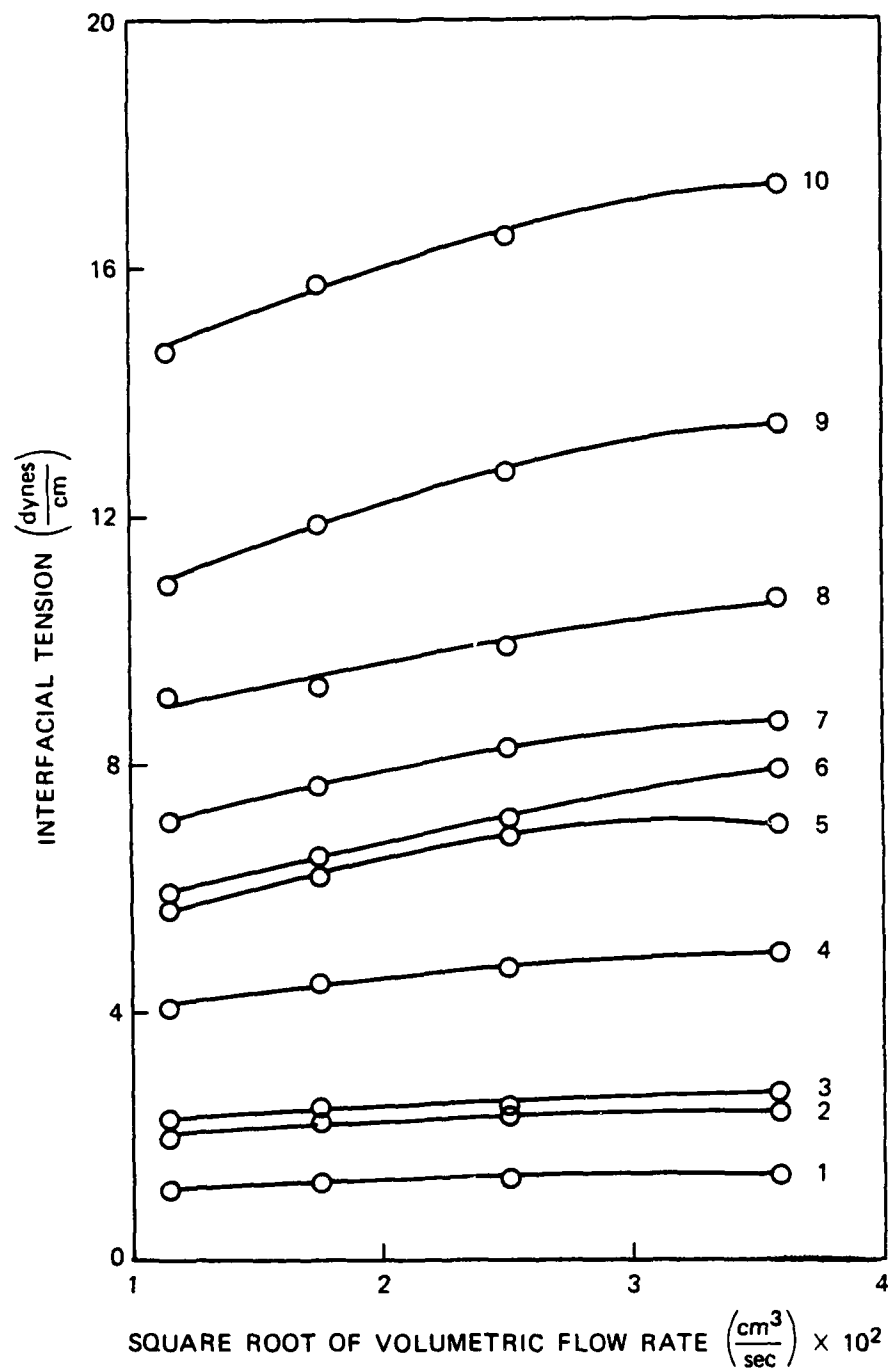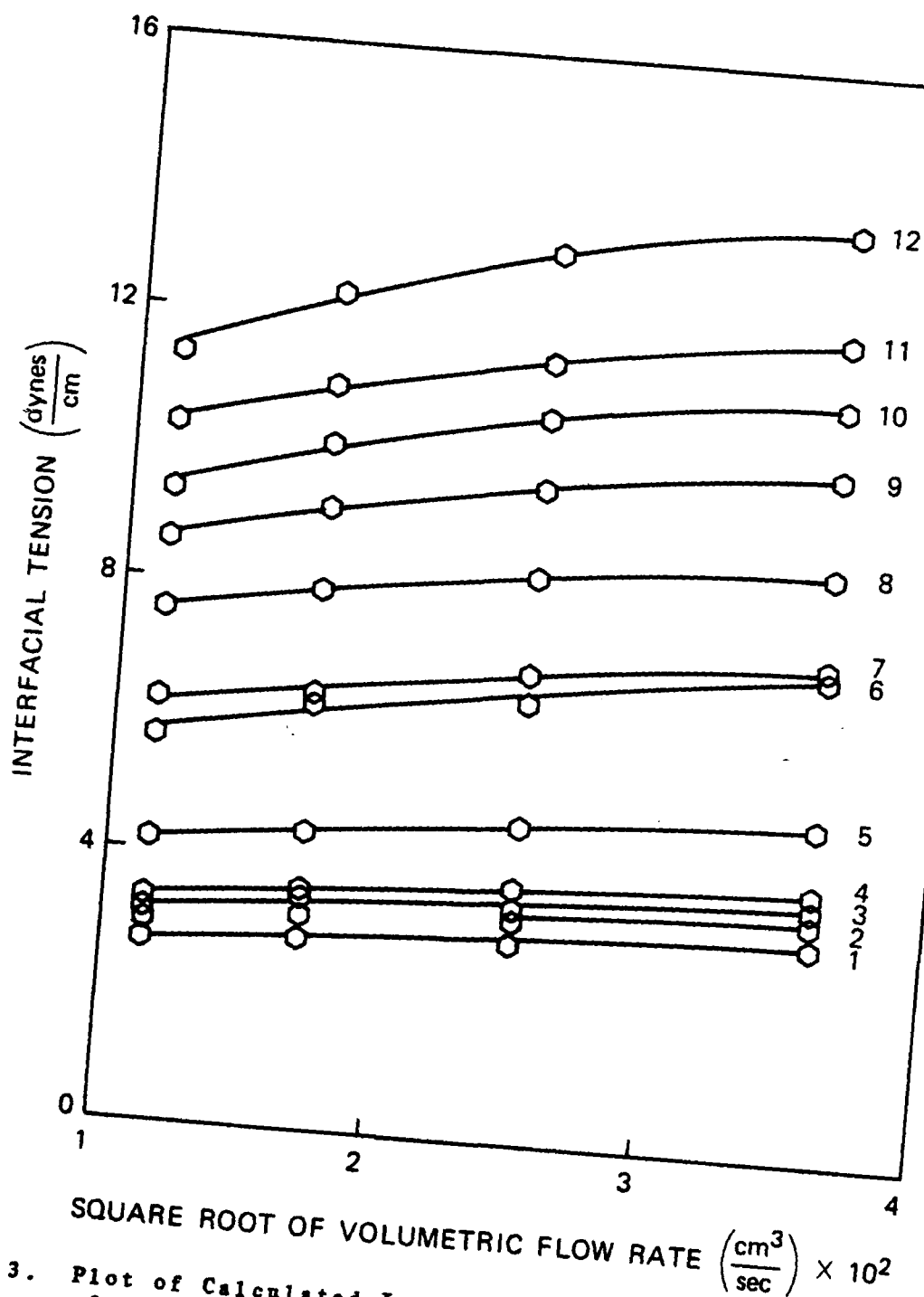Figure 3. Plot of Calculated Interfacial Tension vs. Square Root of Volumetric Flow Rate for Witconate P10-59 Solutions: 1) .17 wt. percent; 2) .14 wt. percent; 3) .13 wt. percent; 4) .11 wt. percent; 5) .08 wt. percent; 6) .06 wt. percent; 7) .058 wt. percent; 8) .046 wt. percent; 9) .036 wt. percent; 10) .028 wt. percent; 11) .023 wt. percent; 12) .014 wt. percent.

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Table 1. Analysis of Aerosol OT Interfacial Tension Data

Conc. Wt. %	$\sqrt{V}$ (cm³/s)	IFT (dynes/cm)	b	IFT$_0$ (dynes/cm)	Correl.
0.007	1.16×10^{-2} 1.73×10^{-2} 2.51×10^{-2} 3.58×10^{-2}	14.6 15.8 16.5 17.4	109	13.7	0.978
0.021	same as above	10.9 11.8 12.7 13.4	102	9.94	0.981
0.037	same as above	9.11 9.27 9.87 10.7	67.5	8.22	0.99
0.047	same as above	7.04 7.63 8.23 8.71	62.9	6.38	0.983
0.053	same as above	5.96 6.56 7.15 7.94	80.2	5.10	0.997
0.063	same as above	5.63 6.20 6.82 7.02	56.9	5.14	0.941
0.100	same as above	4.04 4.47 4.73 4.94	36.4	3.73	0.961
0.240	same as above	2.28 2.42 2.49 2.69	16.1	2.11	0.989
0.270	same as above	1.99 2.21 2.30 2.38	14.9	1.89	0.927
0.700	same as above	1.16 1.27 1.31 1.37	7.98	1.10	0.947

Table 2.   Analysis of Witconate P10-59 Interfacial Tension Data

Conc. Wt. %	$\sqrt{v}$ (cm^3/s)	IFT (dynes/cm)	b	IFT$_0$ (dynes/cm)	Correl.
	1.16×10^{-2}	11.3			
	1.73×10^{-2}	12.3			
0.014	2.51×10^{-2}	13.1	92.4	10.5	0.967
	3.58×10^{-2}	13.7			
	same	10.3			
	as	11.0			
0.023	above	11.5	70.9	9.60	0.979
		12.0			
	same	9.31			
	as	10.1			
0.028	above	10.6	71.2	8.71	0.962
		11.1			
	same	8.59			
	as	9.16			
0.036	above	9.62	60.1	8.02	0.983
		10.1			
	same	7.58			
	as	7.97			
0.046	above	8.33	42.0	7.18	0.979
		8.62			
	same	6.23			
	as	6.43			
0.058	above	6.94	43.4	5.74	0.985
		7.24			
	same	5.68			
	as	6.23			
0.060	above	6.51	58.2	5.10	0.989
		7.17			
	same	4.17			
	as	4.40			
0.080	above	4.66	31.0	3.85	0.994
		4.93			
	same	3.31			
	as	3.56			
0.110	above	3.77	26.9	3.05	0.984
		3.98			
	same	3.12			
	as	3.43			
0.130	above	3.46	23.4	2.92	0.953
		3.75			

Table 2 (continued)

Conc. Wt. %	$\sqrt{v}$ (cm³/s)	IFT (dynes/cm)	b	IFT$_0$ (dynes/cm)	Correl.
	1.16×10^{-2}	2.99			
	1.73×10^{-2}	3.18			
0.140	2.51×10^{-2}	3.32	22.3	2.76	0.994
	3.58×10^{-2}	3.55			
	same	2.69			
	as	2.83			
0.170	above	2.97	19.5	2.48	0.998
		3.17			

Table 3. Extrapolated IFT and Calculated IFT (Equation [5])

$\sqrt{v}$ (cm³/s)	γ_v (dynes/cm)	k_v	γ_0(1) (dynes/cm)	γ_0(2) (dynes/cm)
1.16×10^{-2}	1.16	0.911	1.10	1.06
1.73×10^{-2}	1.27	0.872	same	1.11
2.51×10^{-2}	1.31	0.824	same	1.08
3.58×10^{-2}	1.37	0.767	same	1.05
same	9.31	0.911	8.71	8.47
as	10.1	0.872	same	8.85
above	10.6	0.824	same	8.78
	11.1	0.767	same	8.53
same	14.6	0.911	13.7	13.3
as	15.8	0.872	same	13.7
above	6.5	0.824	same	13.6
	17.4	0.767	same	13.3

(1) Extrapolated value (v = 0) of IFT
(2) Calculated value of IFT from Equation [5]