

Interfacial Properties of a Hydrophobic Dye in the Tetrachlorethylene-Water-Glass Systems

by

D. M. Tuck

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

C. Rulison

RECEIVED
MAR 04 1997
OSTI

DOE Contract No. DE-AC09-96SR18500

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Interfacial Effects of a Hydrophobic Dye in the Tetrachloroethylene-Water-Glass System (U)

David M. Tuck
Christopher Rulison

UNCLASSIFIED

DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

ADC &
Reviewing
Official:

Donna Shedd
(Name and Title)

Date:

11/19/98 *MS*

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

WSRC-TR-97-0038
November 4, 1998
Rev. 0

Interfacial Effects of a Hydrophobic Dye in the Tetrachloroethylene-Water-Glass System (U)

David M. Tuck
Christopher Rulison
(Krüss USA Charlotte, NC)

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

This page intentionally left blank.

Contents

List of Figures	vi
List of Tables	vi
Executive Summary	vii
Introduction	1
Experimental Methods	4
Solutions	4
Interfacial Tension.....	4
Screening Tests Using PCE Lens Thickness	4
Du Noüy Ring Method	5
M-Area DNAPL-Water Interfacial Tension	6
Contact Angle.....	6
Results and Discussion	7
Interfacial Tension.....	7
PCE Lens Thickness Screening Test.....	7
Du Noüy Ring Measurements	7
Drop Volume Measurements.....	7
Contact Angle Measurements	8
Conclusions.....	10
Acknowledgements	10
References.....	11
Appendix A. Krüss USA Report, November 27, 1995	
Appendix B. Wilhelmy Plate Interfacial Tension Measurements of M-Area DNAPL	
Appendix C. Recalculated Drop Volume Interfacial Tension Values	

List of Figures

Figure 1.....	Contact angle illustration	14
Figure 2.....	Distribution of wetting and nonwetting phases in a conical capillary	14
Figure 3.....	Chemical structures of commonly used organic dyes	15
Figure 4.....	General profiles of floating NAPL lenses	16
Figure 5.....	Dyed-PCE-water interfacial tension by drop volume technique	17
Figure 6.....	Lowest measured dyed-PCE-water interfacial tension	18
Figure 7.....	Contact angle between dyed-PCE, water, and glass	19

List of Tables

Table 1.....	Tetrachloroethylene (PCE) solutions and Sudan IV dye concentrations	20
Table 3.....	Mean interfacial tension between undyed PCE and water	21
Table 4.....	Mean interfacial tension between dyed PCE of concentration C4 and water	21
Table 5.....	Mean interfacial tension between dyed PCE of concentration C3 and water	22
Table 6.....	Mean interfacial tension between dyed PCE of concentration C2 and water	22
Table 7.....	Mean interfacial tension between dyed PCE of concentration C1 and water	23
Table 8.....	Contact angle in the Sudan IV-dyed-PCE-water-glass system.	23

EXECUTIVE SUMMARY

Interfacial effects play an important role in governing multiphase fluid behavior in porous media. Strongly hydrophobic organic dyes, used in many experimental studies to facilitate visual observation of the phase distributions, have generally been implicitly assumed to have no influence on the interfacial properties of the various phases in porous media. Sudan IV is the most commonly used dye for non-aqueous phase liquids (NAPLs) in laboratory experiments. It has also been used in at least one field experiment. The effects of this dye on the tetrachloroethylene (PCE)-water-glass system were investigated to test the assumption that the dye does not effect the interfacial properties and therefore PCE mobility. The results indicate that the dye does indeed change the interfacial relationships.

The effect of the dye on the interfacial relationships is a complex function of the dye concentration, the solid phase composition, and the dynamic rate of new interface formation. The dye caused a slight (<10%) increase in interfacial tension at low concentrations (<0.1 g/L) and high rates of new interface formation. The dye reduced interfacial tension between PCE and water at low rates of new interface formation for all dye concentrations tested (0.00508 to 5.08 g/L). At the highest dye concentration, the PCE-water interfacial tension was significantly reduced regardless of the rate of new interface formation. The apparent interfacial tension increase at low dye concentrations is suspected to be an artifact of a low measured IFT value for the undyed PCE caused by leaching of rubber o-rings by the PCE prior to testing in the final drop-volume configuration.

In addition to reducing interfacial tension, the dye was found to significantly alter the wetting relationship between PCE and water on a glass surface at and above the

range of reported dye concentrations cited in the literature (1.1 to 1.7 g/L). The wetting relationship was rendered neutral from a water-wet initial condition at the highest dye concentration. The contact angle, measured through the aqueous phase, changed from 58° for undyed PCE to 93° at a dye concentration of 5.08 g/L. Complete reversal of the wettability is likely given the short equilibration time used in this study (approximately five minutes) together with literature indications that hundreds to thousands of hours may be required to reach equilibrium during contact angle measurements. Observations suggesting changing wetting relationships were also noted between PCE, water, and the platinum-iridium surface used in the standard du Noüy ring method for measuring interfacial tension.

Observations of the dyed-PCE-water interface behavior during du Noüy ring interfacial tension measurements were similar to observations noted previously during measurements of the interfacial tension between the Savannah River Site (SRS) M-Area Settling Basin DNAPL (M-Area DNAPL) and water. This observation suggests that the M-Area DNAPL may contain surface active components. If this proves to be the case, it would have significant implications for how the M-Area DNAPL is distributed and moves in the SRS subsurface.

INTRODUCTION

Interfacial effects play an important role in governing multiphase fluid behavior in porous media [1, 2]. For instance, several dimensionless numbers have been developed to express important force ratios applicable to multiphase flow in porous media [3-7]. The two original numbers used to define these ratios are the capillary number, N_{Ca} , and the Bond number, N_B . The capillary number expresses the ratio of the viscous drag force of a flowing, continuous phase to capillary force acting on a discontinuous phase. The viscous force acts to mobilize the discontinuous phase while the capillary force acts to resist mobilization. In the case of a residual NAPL in a water saturated porous medium, the capillary number is given as

$$N_{Ca} = \frac{\mu_w v_w}{\gamma_{nw}} \quad (1)$$

where μ_w is dynamic viscosity of water (g/cm-sec), v_w is average pore velocity (cm/sec), and γ_{nw} is NAPL-water interfacial tension (dynes/cm, g/sec²). The Bond number expresses the ratio of gravity to capillary forces. The Bond number is expressed as

$$N_B = \frac{(\rho_n - \rho_w)gR^2}{\gamma_{nw}} \quad (2)$$

where ρ_n and ρ_w are the NAPL and water densities (g/cm³), g is the acceleration of gravity (cm/sec²), and R is a characteristic length (cm), generally taken to be the mean grain diameter (cm). In analogy with the capillary number, the gravity forces act to mobilize the discontinuous phase (assuming that a difference in density exists) while the capillary forces resist mobilization.

Both viscous drag forces and gravity forces effect residual NAPL ganglia in

porous media during enhanced recovery processes using surfactants or cosolvents. Thus both forces should, ideally, be considered when evaluating NAPL mobilization potential. Addition of the two force ratios cannot be done directly, however, because of the difference in their magnitudes [3, 8]. Morrow et al. (1988) found it necessary to multiply the bond number by 0.001412 in order to sum the two numbers. Pennell et al. (1996) suggest that the reason for the difference in magnitude between the Bond and capillary numbers is due to a difference in the characteristic length scale over which they are defined. Pennell et al. derived an expression for what they call the total trapping number (N_T) to avoid the empirical nature of the sum as carried out by Morrow et al. The total trapping number is, effectively, a sum of the capillary and Bond numbers, where both are based on the same length scale, the intrinsic permeability of the porous medium. The total trapping number is given by [6]:

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B \sin\alpha + N_B^2} \\ = \frac{2kk_{rw}\beta}{r_n d_b} \quad (3)$$

where α is the angle the flow makes with the positive, horizontal x-axis, k is the intrinsic permeability of the porous medium (cm²), k_{rw} is the relative permeability to the continuous aqueous phase (dimensionless), r_n is a measure of the average pore throat for the medium (cm), d_b is a characteristic ganglion length (cm), and β is a dimensionless number given by

$$\beta = 1 - \frac{r_n}{r_b} \quad (4)$$

where the ratio, r_n/r_b , is a characteristic average ratio of pore throat to pore body radii. For horizontal flow ($\alpha = 0^\circ$), N_T reduces to:

$$N_T = \sqrt{N_{Ca}^2 + N_B^2} \quad (5)$$

For vertical flow ($\alpha = 90^\circ$), N_T reduces to:

$$N_T = |N_{Ca} + N_B| \quad (6)$$

The capillary and Bond numbers in this formulation are defined as follows:

$$N_{Ca} = \frac{q_w \mu_w}{\gamma_{nw} \cos \theta} \quad (7)$$

$$N_B = \frac{(\rho_n - \rho_w) g k k_{rw}}{\gamma_{nw}} \quad (8)$$

where q_w is the Darcy flow velocity of the aqueous phase (cm/sec) and θ is the contact angle between the NAPL-water interface and the solid surfaces of the porous media materials. The total trapping number is thus, in effective, a ratio of a sum of the mobilizing forces (viscous and bouyancy) to the resistive force (capillary). The importance of the force ratios expressed in equations (1) to (6) make knowledge of the fluid-fluid interfacial tension essential when conducting or interpreting experiments on multiphase fluid flow in porous media. Dawson and Roberts [7] derived similar equations to those of Pennell et al. (1996).

Another important consideration in multiphase fluid flow in porous media is the wetting relationship between the fluids and the solid materials. This relationship is generally measured via the contact angle, defined as the angle made between the fluid-fluid interface and the solid surface of the mineral grains. Contact angles are illustrated in Figure 1 for a two different situations, a nonwetting NAPL drop and a wetting NAPL drop. The contact angle represents a mechanical balance between

interfacial tensions at each of the three interfaces. It is defined by the Young equation as follows [9, 10]:

$$\cos \theta = \frac{\gamma_{ns} - \gamma_{ws}}{\gamma_{nw}} \quad (9)$$

where γ_{ns} is the NAPL-solid interfacial tension (dynes/cm, i.e., g/sec²) and γ_{ws} is the water-solid interfacial tension (dynes/cm, i.e., g/sec²). The wetting relationship controls the distribution of the fluid phases in the porous medium. The wetting phase will tend to occupy the pendular region around grain-grain contact points and the smaller pores in the porous medium. This is illustrated in Figure 2. The pressure drop across the fluid-fluid interface is also controlled, in part, by the wetting relationship.

Application of the force ratios expressed in equations (1), (2), (3), (5) and (6) implicitly assumes a uniformly-wet porous medium, i.e., the porous medium is composed of a single solid phase. Generally water is assumed to be the wetting phase, and thus the NAPL exists as residual blobs or ganglia or as "pools" trapped on fine-grained materials which act as barriers to vertical movement. This is the most common assumption made regarding multiphase flow in porous media involving water as one of the fluid phases. Components in either fluid phase that adsorb onto the solid surface can alter the wetting relationship by changing the solid-fluid interfacial tensions, γ_{ns} and γ_{ws} . Water-soluble surfactants are commonly used in solutions to change wetting properties. Jaffé and co-workers [11-15] examined the influence of a nonylphenyl phosphate ester surfactant on PCE mobilization in porous media. This surfactant was found to reverse the wetting relationship between PCE and water on a glass surface [11]. Other researchers have also documented changing wetting relationships with surfactant adsorption onto the solid surface [16, 17]. Thus surface active

components in the aqueous phase can significantly alter the expected distribution of a NAPL in the subsurface. The same is potentially true of surface active components in a NAPL or DNAPL phase. In fact, several researchers have found that NAPL wetting tends to increase with contact time against the solid [18]. This must occur due to sorption of NAPL components at the solid-solution interfaces.

Strongly hydrophobic organic dyes have been used in many experimental studies of multiphase flow to facilitate visual observation of the separate phase distributions [6, 19-23]. Sudan IV is the most commonly used dye for non-aqueous phase liquids (NAPLs) in laboratory experiments [20, 21, 23], and has been used in at least one field experiment [22]. Typical dye concentrations used in these experiments ranged between 1.1 and 1.7 g/L. Of these studies, the only one to mention examining or testing the effect of the dye on the fluid phase behavior was that of Pennell et al. (1996). They reported that an "oil-red-O" dye concentration of 0.0001 M (approximately 0.04 g/L) had "no observable effect" on PCE mobility in the quartz sand media they used.

The objective of this study was to examine the effects of Sudan IV on the interfacial properties of the tetrachloroethylene (PCE)-water-glass system. Interfacial tension was measured as a function of the Sudan IV concentration in PCE. The contact angle made by the PCE-water interface against a flat glass slide was also measured as a function of Sudan IV concentration.

Experimental Methods

Solutions

Sudan IV is an organic dye commonly used for staining NAPLs during multiphase fluid flow studies in porous media [20-23]. The dye was used as received from Eastman Kodak, Inc. The dye structure is illustrated in Figure 3 along with that of a related dye, oil-red-O, which has also been used in multiphase fluid flow studies in porous media [6]. The dye content of the Eastman Kodak sample was 81%. The remaining 19% is inorganic salts, most likely either NaCl or KCl (Aldrich Chemical Company, Inc. 1997, personal communication). The PCE used to prepare all solutions was "Tetrachloroethylene 99%". It was used as received from Mallinckrodt Inc. (Paris, KY). Dyed PCE solutions were prepared by dissolving 0.508 g of the dye, as received, into 100 mL of PCE. Serial dilutions of this stock solution were then prepared. Symbols for the various solutions, and the dye concentrations are presented in Table 1. All solutions were allowed to equilibrate for several days prior to measuring the interfacial properties. The density of all PCE-saturated aqueous phases was 0.9962 g/mL with a standard deviation of 0.0025 g/mL (n = 13).

Interfacial Tension Screening Tests Using PCE Lens Thickness

The effect of the Sudan IV dye on PCE-water interfacial tension was investigated by measuring the maximum thickness of a floating lens of dyed and undyed PCE which could be supported on an air-water interface. The dye concentration was approximately 1.5 g/L. The following equation provides a theoretical estimate of the maximum thickness of a floating PCE lens [24]

$$t^2 = -\frac{2S_{p/w}\rho_w}{g\rho_p\Delta\rho} \quad (10)$$

where ρ_w is the density of water, ρ_p is the density of PCE, $\Delta\rho$ is the density difference between PCE and water, and $S_{p/w}$ is the spreading coefficient of PCE on an air-water interface. $S_{p/w}$ is given by the following equation

$$S_{p/w} = \gamma_{wa} - \{\gamma_{pa} + \gamma_{pw}\} \quad (11)$$

where γ is the interfacial tension between the subscripted phases, and the subscripts are a for air, w for water, and p for PCE. Equation (10) is only applicable if the liquid of the floating lens is non-spreading, i.e., if the spreading coefficient of liquid A (in our case PCE, p) on liquid B (in this case water, w), $S_{A/B}$, is negative. PCE is, in fact, nonspreading on an air-water interface. Surface activity effects of the dye will reduce the surface and interfacial tensions in the quantity in brackets. We assumed the dye effect on the PCE density and PCE-air surface tension was negligible, and therefore that any changes in lens thickness are only a result of changes in the PCE-water interfacial tension. The first assumption is confirmed by the data in Table 1. Surface activity of the dye in the PCE phase would thus result in a smaller lens thickness.

The effect of the dye was tested by carefully adding small additions of PCE (dyed or undyed) to the surface of deionized water in a 50 mL beaker until a drop was released from the floating PCE lens. Lens thickness was measured after each addition of PCE. The lens thickness just prior to release of a drop to the bottom of the beaker was taken to be the equilibrium lens thickness which the water-air interface could support. The thickness of the lens was measured using a mm scale. Figure 4 is a schematic illustration of the lens thickness measurement set-up. The capillary fringe, f_c , of water along the inside edge of the beaker was opaque, optically blocking vision of the full floating lens. The capillary fringe was approximately

3.0 mm thick. PCE lens thicknesses were measured from the base of the capillary fringe to the bottom of the floating lens. The estimated maximum lens thickness, t_{\max} , was obtained by assuming an additional thickness of PCE above the base of the fringe equal to half the capillary fringe thickness, i.e., the estimated maximum thickness was taken to be the sum of the measured thickness in mm plus 1.5 mm. These tests were only used for screening purposes to detect whether the dye changed the surface properties of the PCE-water system. The measurement technique was crude and the lens thickness theory not entirely appropriate since it was formulated for a lens of lower density fluid floating on a higher density fluid, i.e., opposite to the situation here. Therefore interfacial tensions were not calculated from the data. The results were only used as a rapid screening test of whether, in fact the dye had any influence on the PCE-water interfacial tension.

Interfacial Tension by Du Noüy Ring Method

The du Noüy ring technique [25] was applied to measure the interfacial tension between Sudan IV-dyed PCE and water. This work was done using a Krüss Processor Tensiometer K12. The interfacial tension, γ_{nw} , is given by the following equation [26]

$$\gamma_{nw} = \frac{F_{\max} - F_v}{L \cdot \cos\theta} \quad (12)$$

where F_{\max} is the maximum force measured as the tensiometer varies the height of the ring above the interface, F_v is the weight of the volume of liquid directly under the ring, and L is the wetted length of the ring. The contact angle is normally assumed to be zero [26]. The du Noüy ring method also requires corrections for the effect of curvature of the deformed interface inside of the wire ring [24, 26].

Drop Volume Technique

The effect of Sudan IV dye on the PCE-water interfacial tension was also measured using a dynamic drop volume technique. Difficulty was experienced during attempts to measure the "equilibrium" interfacial tension using the standard du Noüy ring and Wilhelmy plate methods [24]. The difficulty occurred because the interface between the dyed PCE and water behaved in an unusual fashion; it would break in an irregular manner while lifting or pushing the platinum ring through the interface. Visual observation indicated that PCE was wetting at least part of the ring, thus violating the complete wetting assumption required for successful application of the ring technique. Dynamic measurements were made instead using the drop volume technique with varying rates of drop formation.

Dynamic interfacial tension between water and the dyed-PCE solutions was measured using a Krüss Drop Volume Tensiometer (model DVT10). The interfacial tension was measured as a function of the PCE flow rate from a precision syringe pump into the water phase through a specially designed alumina tip. The PCE drops were counted by an optical system which is part of the tensiometer. The drop volumes were determined by the pump rate and the length of time between successive drops. The interfacial tension is computed from the drop volume using the following equation [27]:

$$\gamma_{nw} = \frac{V_D \Delta\rho g}{\pi d} \quad (13)$$

where γ_{nw} is the NAPL-water interfacial tension, V_D is the volume of the drop, $\Delta\rho$ is the density difference between the two fluids, g is the gravitational acceleration, and d is the diameter of the tip from which the drop is suspended. More details on the measurement system are contained in Appendix A.

M-Area DNAPL-Water Interfacial Tension

measured through the PCE phase (see Figure 5 of Appendix A).

A sample of the M-Area DNAPL and an associated colloidal emulsion was obtained from well MSB-3D in June 1994. A subsample was placed in a 40 mL vial. After settling for approximately 20 days, this subsample segregated into three "phases": a high density, light brown, translucent phase (hereafter referred to as the "pure" M-Area DNAPL), an intermediate density, milky white emulsion, and a well-equilibrated aqueous phase. The composition of the "pure" M-Area DNAPL is estimated to be approximately 95 % PCE and 5% TCE (trichloroethylene) [28]. The Wilhelmy plate method [24; 26] was used to measure the interfacial tension between the "pure" M-Area DNAPL phase (i.e., without any colloidal phase present) and the well-equilibrated aqueous phase collected with the sample. A glass pipette was inserted below the emulsion to collect the sample of "pure" M-Area DNAPL. A fresh, clean glass pipette was used to collect a sample of the well-equilibrated aqueous phase for the interfacial tension analysis. Additional measurements were made between the "pure" M-Area DNAPL and a sample of clean tap water. The interfacial tension was also measured using the du Noüy ring method for this later pair of liquids.

Contact Angle

The wetting relationships between Sudan IV-dyed PCE and water on a glass surface were examined by measuring contact angle as a function of the dye concentration. Contact angles were measured using a Krüss Goniometer (model G10). For each concentration, a drop of the dyed PCE was placed on a glass slide which had been submerged in water pre-equilibrated with undyed PCE. The drop was allowed to equilibrate on the glass surface for approximately five minutes. The contact angle was then

Results and Discussion

Interfacial Tension PCE Lens Thickness Screening Test

The PCE lens thickness measurements are presented in Table 2. A t-test was conducted to determine whether the difference observed in the two sample means was significant [29]. The calculated t-statistic from the experimental data is 3.52. Critical values of the t-distribution with five degrees of freedom are 3.365 for $p = 0.02$ and 4.032 for $p = 0.01$. The means are therefore statistically significantly different at a confidence level of 98%. Thus the dye appeared to have a significant effect on the PCE-water interfacial tension.

Further testing was therefore needed to characterize the magnitude of the effect on the interfacial tension as a function of dye concentration. This test is not sufficiently sensitive to quantify the interfacial tension reduction as a function of the dye concentration.

Du Noüy Ring Interfacial Tension Measurements

Difficulties were encountered when the du Noüy ring method was applied to dyed PCE. Slow changes in the measured interfacial tension were observed. In addition, the interface between the dyed PCE and water behaved in an unusual fashion; it would break in an irregular manner while lifting or pushing the platinum ring through the interface. These same behaviors occurred whether the ring was pushed down from the aqueous phase into the PCE phase or was pulled up through the interface. Visual observations suggested that the wetting relationship between PCE, water, and the platinum ring was not constant, but was changing with time. This type of behavior on platinum has been noted by other researchers [30]. The change in

wetting violates the assumptions of the measurement technique, rendering any results suspect. Hence the results are not reported here.

In June 1994, interfacial tension was measured between SRS tap water and a sample of the M-Area DNAPL obtained from well MSB-3D. Similar interfacial behavior was noted during those measurements, including one-directional changes in interfacial tension and irregular breaking of the interface during du Noüy ring measurements. The best results achieved during those measurements were attained using the Wilhelmy plate method with the well-equilibrated well water [24]. The mean interfacial tension was 9.592 mN/m with a standard deviation of 0.006 mN/m ($n=10$, see Appendix B).

Drop Volume Interfacial Tension Measurements

Water was initially pumped upward into a continuous PCE phase to measure the interfacial tension. Continually decreasing values of interfacial tension were obtained at the same flow rate. This suggested that the PCE was leaching components from the rubber o-ring used to seal the apparatus. Cracks were observed in the o-ring when the system was disassembled, confirming this assessment. Similar results were attained when an o-ring made of a more solvent-resistant material (Kalrez) was used in the device under the same configuration of pumping water up into the PCE phase, although the magnitude of change was significantly lower. Consequently, the system was switched to pumping PCE down into a continuous water phase. The PCE tended to wet a tungsten-carbide tip that was used initially in this configuration. The PCE tendency to partially wet a metal surface was consistent with the results observed on the platinum ring. This situation violates the assumptions of the equation applied to calculate interfacial tension. An alumina tip alleviated the PCE wetting problem.

Water remained the wetting solution in all the remaining tests.

The mean interfacial tension results between Sudan IV-dyed PCE and water are given as a function of the PCE flow rate in Tables 3 to 7 for the different dye concentrations. PCE flow rate is roughly proportional to the rate of new interface formation. Interfacial tensions, corrected for the PCE and aqueous solution density, were calculated from the raw drop volume data in Appendix A along with the fluid density data in Table 1 using equation (13). These calculations are presented in Appendix C. In all cases the interfacial tension decreases as the PCE flow rate decreases. The results are illustrated in Figure 5 as a function of flow rate. The undyed PCE-water interfacial tension leveled off at approximately 45.89 dynes/cm (mN/m) at the lowest two flow rates applied for that system, 0.5 mL/hr and 0.25 mL/hr. This value is thought to be low due to incorporation of rubber components leached during the initial attempts to measure IFT when the undyed PCE was in contact with a rubber o-ring.

The IFT of the lowest dye concentration solution, C4 = 0.00508 g/L, also appeared to level off, but at a lower value of approximately 40.3 dynes/cm (mN/m) and at lower PCE flow rates, 0.1 mL/hr and 0.05 mL/hr. The interfacial tensions of all the remaining solutions of higher dye concentration appeared to still be decreasing with decreasing flow rate even at the lowest applied flow rate of 0.05 mL/hr. At the lower dye concentrations, less than or equal to 0.5 g/L, the dye appeared to increase the interfacial tension at the higher flow rates. This apparent IFT increase is thought to be due to contamination of the undyed PCE by leaching rubber components as discussed above. At the highest dye concentration, 5.08 g/L, all interfacial tension results were significantly less than the results for the undyed-PCE-water system. Figure 6 contains plots of the lowest measured interfacial tension as a function of the dye concentration and the interfacial tension

measured at a PCE flow rate of 0.25 mL/hr (the lowest flow rate used with the undyed PCE). The lowest interfacial tension results suggest that Sudan IV reduces the PCE-water interfacial tension even at the lowest dye concentration tested. These results are consistent with literature observations that dynamic methods of interfacial tension measurement tend to yield high interfacial tension values for solutions [24, 31].

Contact Angle Measurements

Contact angle results for the Sudan IV dyed PCE with respect to water are given in Table 8. At the lower three dye concentrations, the dye appeared to increase the hydrophobic/non-polar nature of the PCE phase. The contact angles measured through the PCE phase increased, indicating that the aqueous phase was relatively more wetting on the glass surface than was the case for undyed PCE. At the highest concentration, however, the wetting relationship was rendered neutral; contact angle decreased to $87^\circ \pm 3^\circ$. Two additional solutions were prepared to examine the contact angle behavior at concentrations between 5.08 and 0.508 g/L. Dilutions of the C1 PCE solution were prepared to yield dye concentrations of approximately 1.27 g/L in solution C1.2 and 1.69 g/L in solution C1.6. The contact angles for these solutions also indicated that significant changes occurred in the wetting behavior. The contact angles were $70^\circ \pm 3^\circ$ in C1.2 and $75^\circ \pm 3^\circ$ in C1.6. The contact angle measured through the aqueous phase is plotted as a function of dye concentration in Figure 7. The wetting relationship clearly changes as the dye concentration increases.

NAPL wetting has been shown to increase with time of exposure to the solid surface for complex NAPLs characteristic of natural or refined oil [18, 32], presumably due to adsorption and/or deposition of organic matter onto the solid surface. As a result, Anderson

[33], has suggested that equilibrium contact angle measurements involving NAPLs containing surface active agents may require aging for hundreds to thousands of hours. It is therefore likely that, given longer equilibration time, the dyed PCE could become the wetting phase, even at lower dye concentrations, based on these previous literature results together with the fact that only a very short equilibration time (approximately 5 minutes) was used during this study. Recent experimental evidence supports this prediction [34].

Reversal of the wetting relationship has major implications for DNAPL mobility in the saturated subsurface. First, the wettability relationship controls the fluid phase distribution in the subsurface as illustrated in Figure 2 [10]. Therefore, as the wetting relationship changes, so the fluid phase distribution will change. Second, the mechanism of DNAPL migration into fresh, uncontaminated areas will change as the wettability relationship changes. DNAPL moves pore-to-pore via piston-type displacement governed by the capillary and Bond number force ratios when it is non-wetting with respect to the aqueous phase. As the DNAPL becomes the wetting phase, however, it may begin to migrate via thin-film flow [34, 35]. The ultimate result of changing the wetting relationship is that the concept of a permanent capillary barrier to DNAPL migration may not fully represent reality in the subsurface. The surface chemical reactions of complex DNAPLs need to be investigated with respect to different sedimentary minerals in order to assess the importance of this topic to understanding DNAPL behavior in the subsurface. Currently little or no such information is available.

CONCLUSIONS

Sudan IV dye has significant influences on interfacial properties of the PCE-water-glass system. At concentrations greater than approximately 0.05 g/L it begins to reduce the interfacial tension between water and the dyed PCE. This will therefore result in a decreased capillary force resisting mobility of the PCE phase. In addition, at concentrations greater than 1 g/L the dye can significantly alter the wetting relationship between the fluid phases. The wetting relationship may change significantly even at lower dye concentrations. This prediction has been confirmed experimentally, and is further supported by slow changes in wetting relations noted in the literature [18, 32]. These results indicate the importance of testing the effects of dyes prior to using them in experimental systems. The interfacial effects of the dye also suggest that previous experimental results obtained using Sudan IV-dyed DNAPLs should be used with caution or perhaps be re-interpreted.

The similarity noted between behavior of the dyed-PCE-water interface and the M-Area DNAPL-water interface during du Nouÿ ring method interfacial tension measurements suggests that the dye makes PCE behave in a fashion similar to that observed with the M-Area DNAPL. The possibility of altered wetting relationships caused by components of the DNAPL would have significant implications for how the M-Area DNAPL is distributed and moving in the SRS subsurface. This possibility should be examined experimentally. Specifically, experimental work is required to 1) identify what types of DNAPL components possess surface active characteristics, 2) examine the surface chemistry of model DNAPL surface active components at both the DNAPL-water interface and at the DNAPL-mineral surfaces, and 3) evaluate the mobility of surface-active DNAPLs in the

subsurface, particularly with respect to the major mechanism of movement.

Acknowledgements

The information contained in this report was developed during the course of work under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy. Funding was provided by the Office of Science & Technology under TTP No. SR-1410-10.

REFERENCES

1. Neustadter, E.L. "Surfactants in enhanced oil recovery" in *Surfactants*, T.F. Tadros, Editor. p. 277-285. Academic Press, Inc., New York. (1984).
2. Tuck, D.M., *et al.* "Enhancing recovery of immobile residual non-wetting hydrocarbons from the unsaturated zone using surfactant solutions". *NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*. Houston, TX: National Water Well Association. pp. 457-478. (1988).
3. Morrow, J.C. and B. Songkran. "Effects of viscous and bouyancy forces on non-wetting phase trapping in porous media" in *Surface Phenomena in Enhanced Oil Recovery*, D.O. Shah, Editor. p. 387-411. Plenum Press, New York. (1981).
4. Chatzis, I. and N.R. Morrow. "Correlation of capillary number relationships for sandstone". *Society of Petroleum Engineers Journal* 24, p. 555-562 (1984).
5. Wardlaw, N.C. "Fluid topology, pore size and aspect ratio during imbibition". *Transport in Porous Media* 3, p. 17-34 (1988).
6. Pennell, K.D., G.A. Pope, and L.M. Abriola. "Influence of viscous and bouyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing". *Environmental Science & Technology* 30, p. 1328-1335 (1996).
7. Dawson, H.E. and P.V. Roberts. "Influence of viscous, gravitational, and capillary forces on DNAPL saturation". *Ground Water* 35, p. 261-269 (1997).
8. Morrow, N.R., I. Chatzis, and J.J. Taber. "Entrapment and mobilization of residual oil in bead packs". *SPE Reservoir Engineering* 3, p. 927-934 (1988).
9. Young, T. "An essay on the cohesion of fluids". *Philosophical Transactions of the Royal Society (London)* 95, p. 65-87 (1805).
10. Dullien, F.A.L. *Porous Media: Fluid Transport and Pore Structure*. 2nd ed. pp. 574. Academic Press, Inc., San Diego. (1992).
11. Hohmann, J.D. *Toward Mobilizing tetrachloroethylene (PCE) in contaminated aquifers: laboratory contact angle studies*. Junior Thesis, Princeton University. (1987).
12. Jaffé, P.R., *et al.* *Investigation of Residual Solvent Recovery in Soils Using Surfactants, prepared for the N.J. Department of Environmental Protection*. 89-WR-1. Princeton University, Water Resources Program, Princeton, NJ., (1989).
13. Jaffé, P.R., D.M. Tuck, and J. Zou. *Solvent Recovery in Soils Using Surfactants; Part II, prepared for the N.J. Department of Environmental Protection*. 91-WR-1. Princeton University, Water Resources Program, Princeton, NJ., (1991).
14. Tuck, D.M. *Immiscible displacement of residual tetrachloroethylene from saturated and unsaturated porous media*. Ph. D. Thesis, Princeton University. (1992).

15. Tuck, D.M. and P.R. Jaffé. "Enhanced displacement of tetrachloroethylene from unsaturated sediments by surfactant solutions". *207th American Chemical Society National Meeting*. San Diego, CA: American Chemical Society Division of Environmental Chemistry (preprints of Papers Series). pp. 632. (1994).
16. Gau, C.-S. and G. Zografis. "Relationships between adsorption and wetting of surfactant solutions". *Journal of Colloid and Interface Science* 140, p. 1-9 (1990).
17. Varadaraj, R., et al. "Relationships between dynamic contact angle and dynamic surface tension properties for linear and branched ethoxylate, ethoxysulfate, and sulfate surfactants". *Journal of Colloid and Interface Science* 147, p. 403-406 (1991).
18. Cohen, R.M. and J.W. Mercer. *DNAPL Site Evaluation*. pp. 339. C.K. Smoley, Boca Raton, FL. (1993).
19. Schwille, F. *Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments*. pp. 146. Lewis Publishers, Inc., Chelsea, MI. (1988).
20. Kueper, B.H., W. Abbott, and G. Farquhar. "Experimental observations of multiphase flow in heterogeneous porous media". *Journal of Contaminant Hydrology* 5, p. 83-95 (1989).
21. Kueper, B.H. and E.O. Frind. "Two-Phase flow in heterogeneous porous media 2. Model application". *Water Resources Research* 27, p. 1059-1070 (1991).
22. Kueper, B.H., et al. "A field experiment to study the behavior of tetrachloroethylene below the water table: Spatial distribution of residual and pooled DNAPL". *Ground Water* 31, p. 756-766 (1993).
23. Brewster, M.L., et al. "Observed migration of a controlled DNAPL Release by Geophysical Methods". *Ground Water* 33, p. 977-987 (1995).
24. Adamson, A.W. *Physical Chemistry of Surfaces*. 5 ed. pp. 777. John Wiley & Sons Inc., New York. (1990).
25. ASTM. "ASTM D1331-89. Standard test method for surface and interfacial tension of solutions of surface-active agents" in *1994 Annual Book of ASTM Standards*. p. 116-118. American Society for Testing and Materials, Philadelphia. (1994).
26. Gilman, L.B. "A review of instruments for static and dynamic surface and interfacial tension measurement". *84th AOCS Annual Meeting and Exposition*. Anaheim, CA: Reprint from Kruss USA, Charlotte, NC. pp. 18 pp. (1993).
27. Tate, T. "On the magnitude of a drop of liquid formed under different circumstances". *Philosophical Magazine* 27, p. 176-180 (1864).
28. Looney, B.B., et al. *Assessing DNAPL Contamination, A/M-Area, Savannah River Site: Phase I Results*. WSRC-RP-92-1302. Westinghouse Savannah River Company, Aiken, SC, (1992).

29. Burington, R.S. and D.C. May Jr. *Handbook of Probability and Statistics with Tables*. pp. 332. Handbook Publishers, Inc., Sandusky, OH. (1953).
30. Gaonkar, A.G. and R.D. Neuman. "The effect of wettability of Wilhelmy plate and du Noüy ring on interfacial tension measurements in solvent extraction systems". *Journal of Colloid and Interface Science* 98, p. 112-119 (1984).
31. Padday, J.F. and D.R. Russell. "The measurement of the surface tension of pure liquids and solutions". *Journal of Colloid Science* 15, p. 503 (1960).
32. Treiber, L.E., D.L. Archer, and W.W. Owens. "A laboratory evaluation of the wettability of fifty oil producing reservoirs". *Society of Petroleum Engineers Journal* 12, p. 531-540 (1972).
33. Anderson, W.G. "Wettability Literature Survey-Part 2: wettability measurement". *Journal of Petroleum Technology* 38, p. 1246-1262 (1986).
34. Pirkle, W.A., G.M. Iversen, and D.M. Tuck. *The effect of an organic dye on DNAPL entry pressure into water saturated porous media. Final report submitted in completion of SCUREF Project SC-0001-EC, SCUREF Task 185, Phase II.* University of South Carolina-Aiken, (1997).
35. Tuck, D.M., G.M. Iversen, and W.A. Pirkle. "Complex Organic Co-contaminant Effects on DNAPL Mobility in Saturated Porous Media". *Eos* 77, p. F257 (1996).

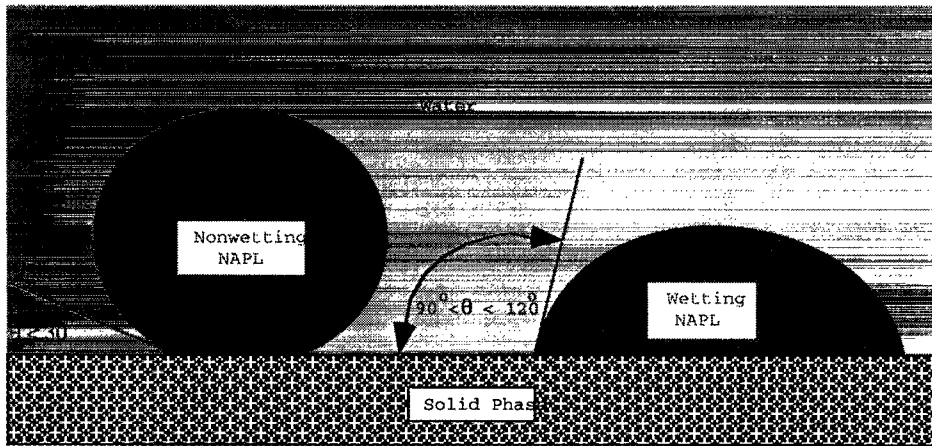


Figure 1. Contact angle illustration. Left side illustrates a strongly water-wet condition ($\theta < 30^\circ$). Right side illustrates a weakly NAPL-wet condition ($90^\circ < \theta < 120^\circ$).

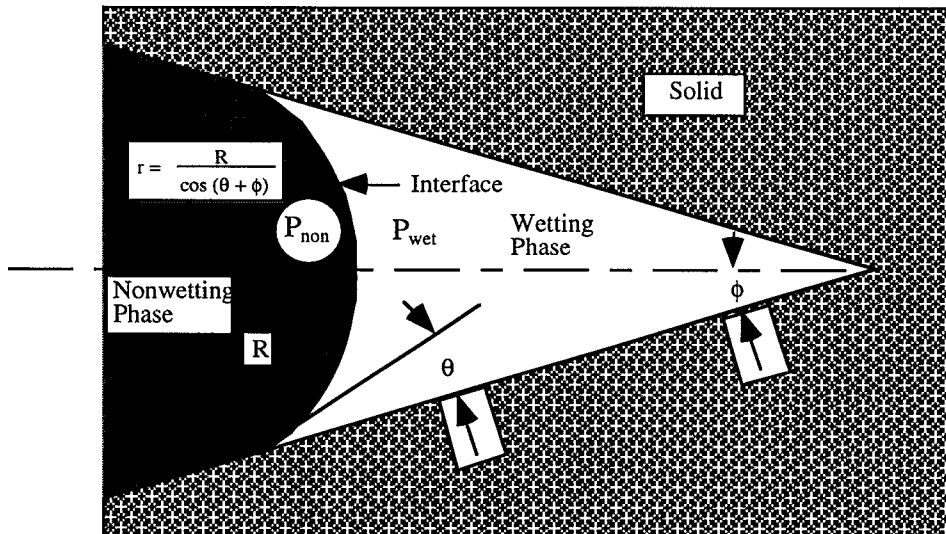


Figure 2. Relative distribution of the wetting and nonwetting phases in a conical capillary. (modified after [10])

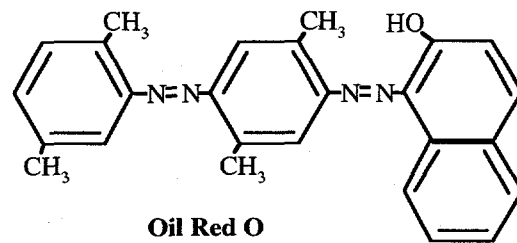
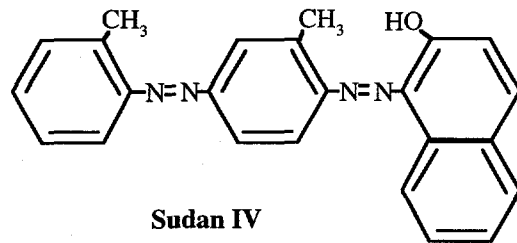
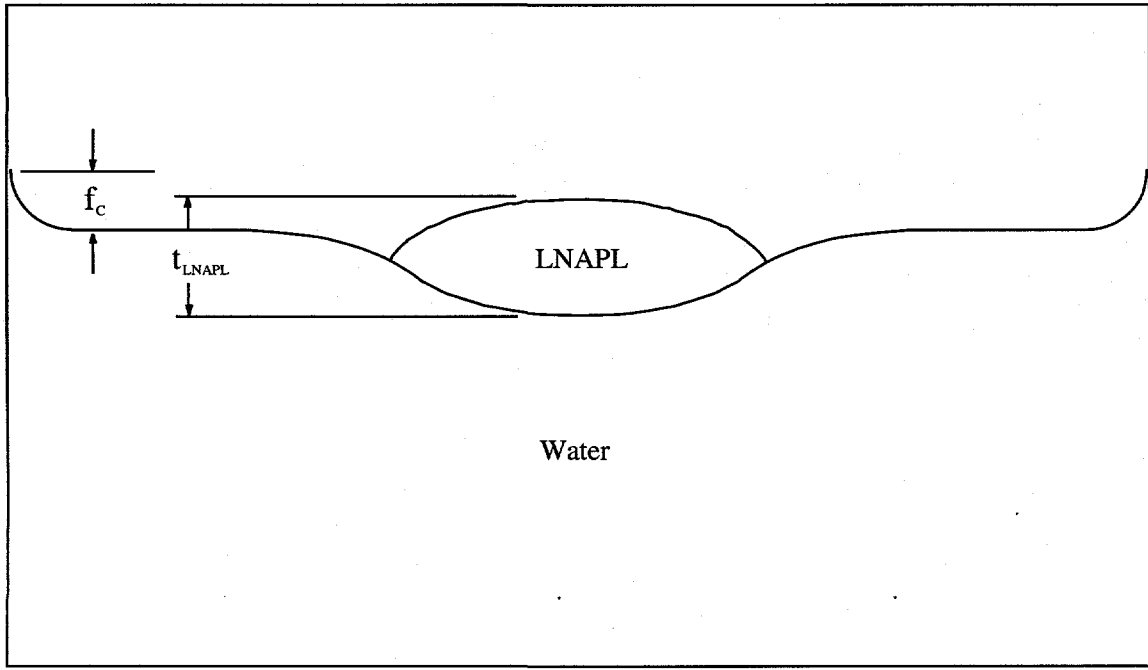
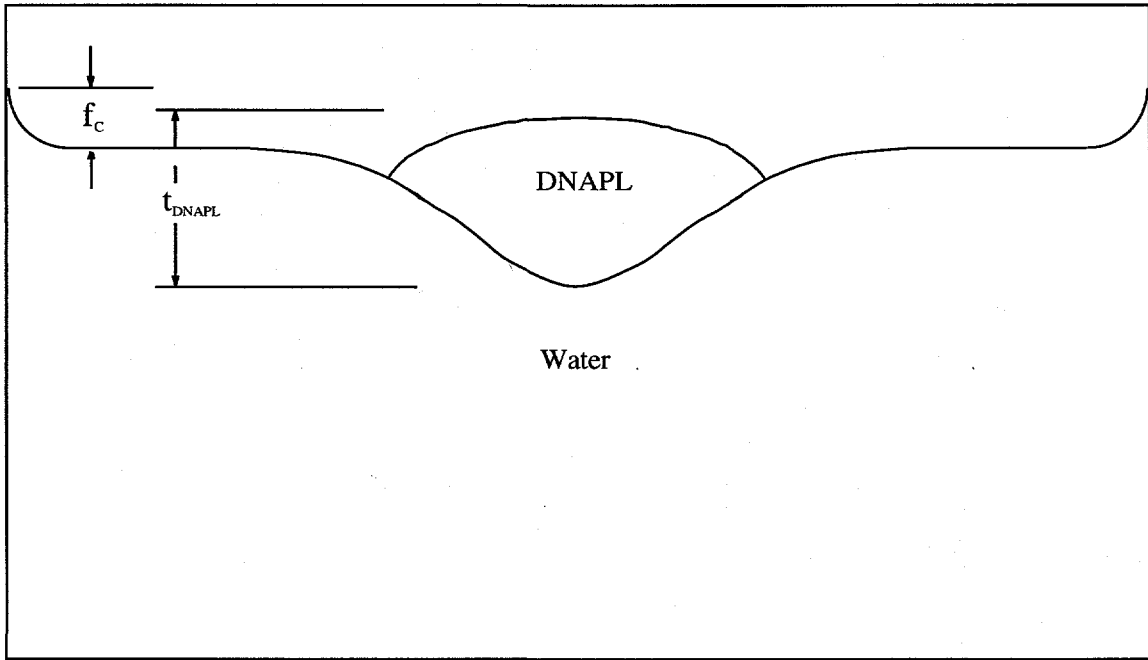


Figure 3. Chemical structures of organic dyes commonly used in multiphase flow visualization studies.



a.



b.

Figure 4. General profiles of floating NAPL lenses. The symbol f_c represents the thickness of the water capillary fringe in contact with the glass beaker. a. NAPL with density less than water, i.e., an LNAPL. b. NAPL with density greater than water, i.e., a DNAPL.

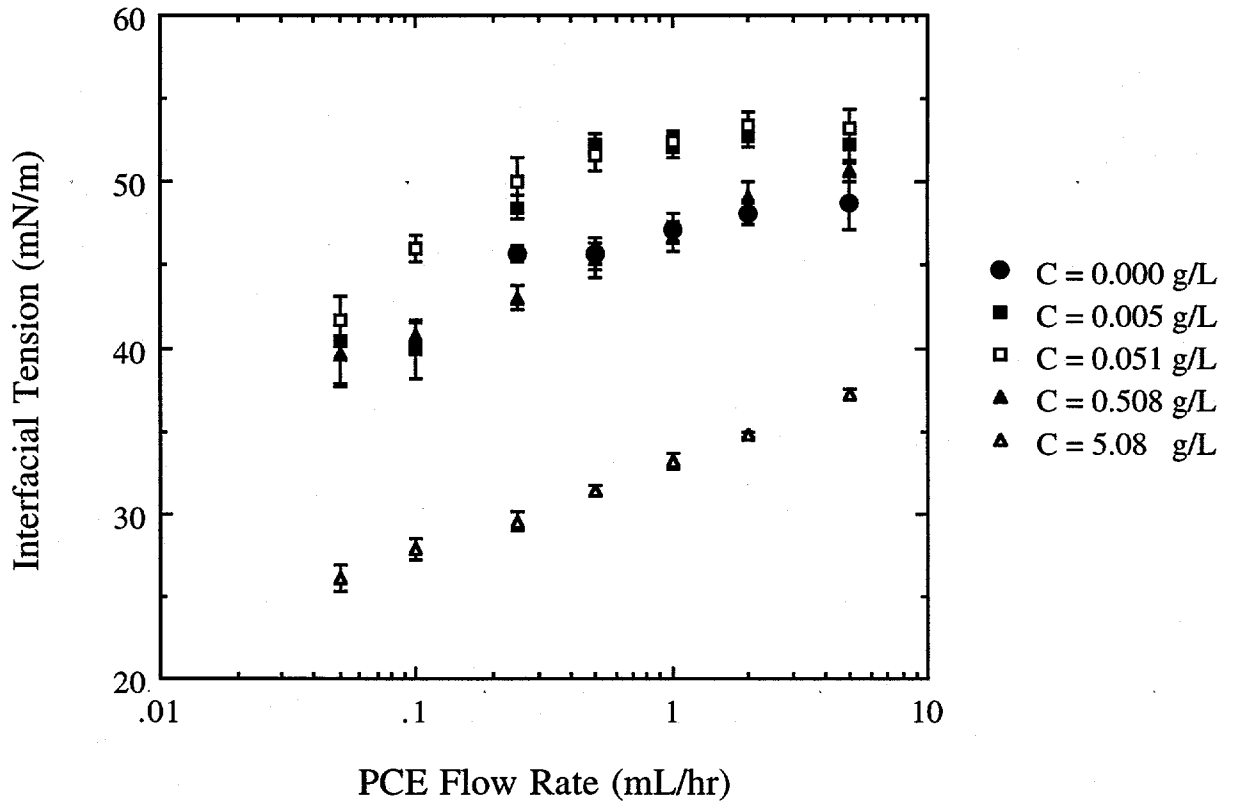


Figure 5. Dyed-PCE-water interfacial tension by drop volume technique as a function of PCE flow rate.

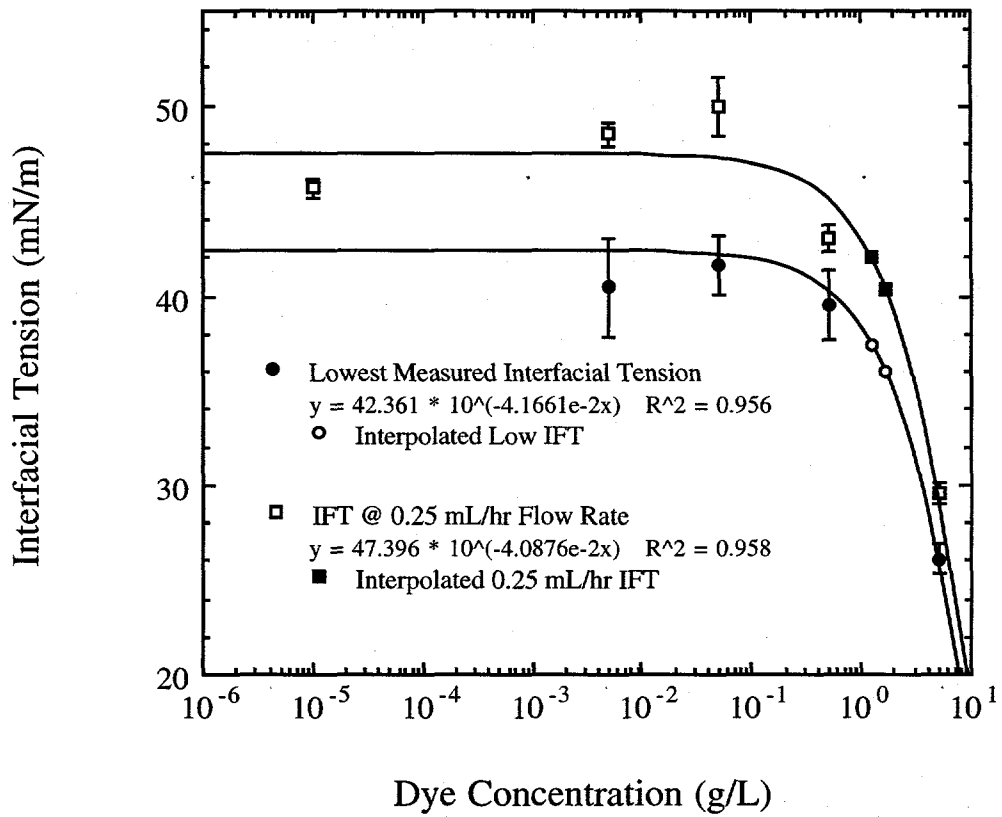


Figure 6. Lowest dyed-PCE-water interfacial tension measured by the drop volume technique. Data points for 1.26 g/L and 1.69 g/L were estimated by interpolation.

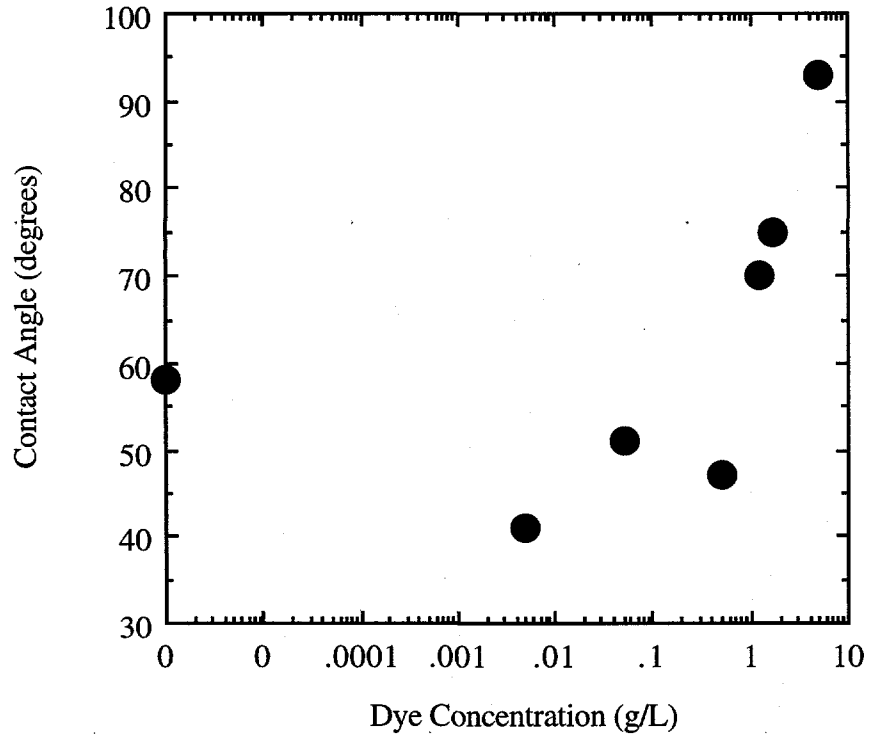


Figure 7. Contact angle between dyed-PCE, water, and glass measured through the water phase.

Solution ID	Sudan IV Dye Concentration (g/L)	Solution Density (g/mL)
C0	0.00000	1.6153
C4	0.00508	1.6150
C3	0.0508	1.6158
C2	0.508	1.6147
C1.27	1.27	1.6145
C1.69	1.69	NA
C1	5.08	1.6141

Table 1. Tetrachloroethylene (PCE) solutions and Sudan IV dye concentrations. NA indicates that the density was not measured.

Lens Thickness without Sudan IV Dye (mm)	Lens Thickness with ~1.5 g/L Sudan IV Dye (mm)
6.0	5.5
6.2	5.5
6.5	
6.0	
6.5	

Table 2. Floating PCE lens thickness measurements.

PCE Syringe Pump Rate (mL/hr)	Mean Interfacial Tension (mN/m)	Standard Deviation (mN/m)	Number of Drops
5.00	48.75	1.64	10
2.00	48.16	0.74	10
1.00	47.22	0.92	10
0.5	45.66	0.94	10
0.25	45.67	0.51	10

Table 3. Mean interfacial tension between undyed PCE and water as a function of flow rate.

PCE Syringe Pump Rate (mL/hr)	Mean Interfacial Tension (mN/m)	Standard Deviation (mN/m)	Number of Drops
5.00	51.99	1.38	10
5.00	52.60	1.18	10
5.00	52.75	1.00	8
2.00	52.691	0.490	10
1.00	52.189	0.700	10
0.50	52.189	0.700	10
0.25	48.502	0.655	10
0.10	39.849	1.639	10
0.05	40.480	2.623	5

Table 4. Mean interfacial tension between PCE and water as a function of flow rate for Sudan IV dye concentration $C_4 = 0.00508$ g/L in PCE.

PCE Syringe Pump Rate (mL/hr)	Mean Interfacial Tension (mN/m)	Standard Deviation (mN/m)	Number of Drops
5.00	53.29	1.07	10
2.00	53.40	0.88	10
1.00	52.49	0.61	10
0.50	51.66	0.97	10
0.25	49.98	1.57	10
0.10	46.05	0.75	5
0.05	41.65	1.50	5

Table 5. Mean interfacial tension between PCE and water as a function of flow rate for Sudan IV dye concentration $C_3 = 0.0508$ g/L in PCE.

PCE Syringe Pump Rate (mL/hr)	Mean Interfacial Tension (mN/m)	Standard Deviation (mN/m)	Number of Drops
5.00	50.68	0.65	10
2.00	49.08	1.03	10
1.00	46.70	0.88	10
0.50	45.35	1.03	10
0.25	43.04	0.70	10
0.10	40.68	1.02	5
0.05	39.52	1.79	6

Table 6. Mean interfacial tension between PCE and water as a function of flow rate for Sudan IV dye concentration $C_2 = 0.508$ g/L in PCE.

PCE Syringe Pump Rate (mL/hr)	Mean Interfacial Tension (mN/m)	Standard Deviation (mN/m)	Number of Drops
5.00	37.19	0.38	10
2.00	34.78	0.17	10
1.00	33.18	0.45	10
0.50	31.39	0.37	10
0.25	29.51	0.56	10
0.10	27.89	0.65	6
0.05	26.08	0.80	5

Table 7. Mean interfacial tension between PCE and water as a function of flow rate for Sudan IV dye concentration $C_1 = 5.08$ g/L in PCE.

Dye Concentration (g/L)	Contact Angle through PCE (degrees)	Estimated Maximum Error (degrees)	Contact Angle through Water (degrees)
0.00000	122	3	58
0.00508	139	3	41
0.0508	129	3	51
0.508	133	3	47
1.27	110	3	70
1.69	105	3	75
5.08	87	3	93

Table 8. Contact angle in the Sudan IV-dyed-PCE-water-glass system.

Appendix A.

Krüß USA Report

prepared by

Dr. Christopher Rulison

November 27, 1995

Sample Analysis Report

Prepared for: David Tuck, Ph.D. - Westinghouse Savannah River Company

Prepared by: Christopher Rulison, Ph.D. - Krüss USA

Date: November 27, 1995

Background

On November 13th and 14th, tests were performed on the following samples at Krüss USA in Charlotte, North Carolina.

C1 - A 5.08g/L solution of dye in perchloroethylene which was pre-equilibrated with water

C2 - A 0.508g/L solution of dye in perchloroethylene which was pre-equilibrated with water

C3 - A 0.0508g/L solution of dye in perchloroethylene which was pre-equilibrated with water

C4 - A 0.00508g/L solution of dye in perchloroethylene which was pre-equilibrated with water

PCE - "Pure" perchloroethylene which was pre-equilibrated with water

X1 - A mixture of 1 part C1 and 3 parts PCE, thus producing a perchloroethylene solution with a dye concentration of 1.27g/L

X2 - A mixture of 1 part C1 and 2 parts PCE, thus producing a perchloroethylene solution with a dye concentration of 1.69g/L

D1 - A two phase system containing approximately 23% Dowfax C6L (sodium hexyl diphenyloxide disulfonate), water, and perchloroethylene

D2 - A pre-equilibrated two phase system containing 9.14% Dowfax C6L, water, and perchloroethylene

D3 - A pre-equilibrated two phase system containing 4.57% Dowfax C6L, water, and perchloroethylene

D4 - A pre-equilibrated two phase system containing 1.828% Dowfax C6L, water, and perchloroethylene

Drop volume tests

The series {PCE, C1, C2, C3, C4} was tested for dynamic interfacial tension against the water (with which it was pre-equilibrated) using a Krüss Drop Volume Tensiometer (DVT10). A variety of flow rates were studied, and three fundamentally different drop volume designs were employed. For each test the density of the perchloroethylene phase was assumed to be 1.62g/cm³ and the density of the aqueous phase was assumed to be 0.998g/cm³.

The principle of drop volume interfacial tensiometry is that the interfacial tension (the energy per unit area necessary to expand the region of contact) between two immiscible liquids can be determined from a balance of the forces which act on a drop of one of the liquids suspended in a continuous phase of the other liquid. Much of the credit for the development of this concept is attributed to Tate¹ who more than a century ago introduced the equation:

$$\gamma = \frac{V_D \Delta\rho g}{\pi d}$$

where γ = the interfacial tension between the liquids, V_D = the volume of the drop, $\Delta\rho$ = the difference in density between the drop liquid and the continuous liquid, g = gravity, d = the diameter of the tip on which the drop is suspended, and π has its standard mathematical meaning.

Since it is a balance of the forces acting on a drop in the upward and downward directions, this form of Tate's equation only applies to a drop on a thin walled capillary tip which is precisely at the volume required for spontaneous detachment. See figure 1, which is a schematic representation of a drop formed on a syringe tip in a drop volume experiment.

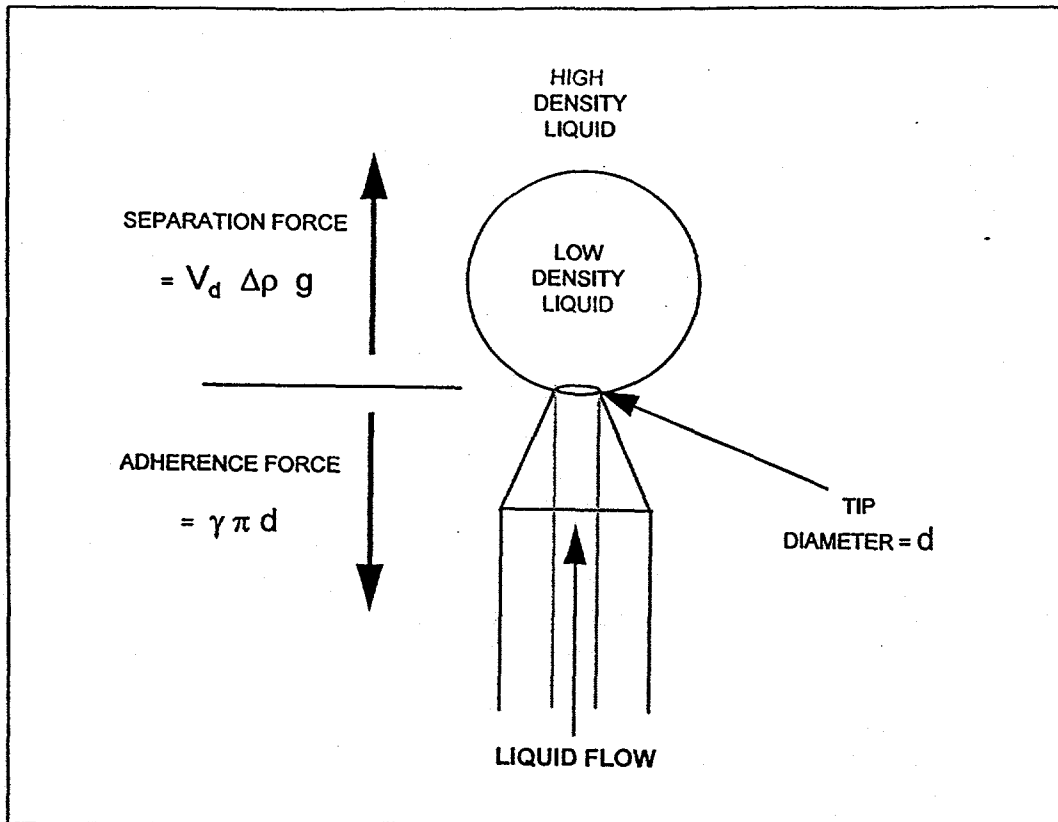


Figure 1

Assume that the drop in figure 1 is formed on a proper capillary and has the precise volume at which Tate's law applies. If the drop had any more volume, the separation force would overcome the adherence force and the drop would detach from the tip and rise through the continuous phase. If the drop had less volume, the adherence force would be greater than the separation force and the drop would not spontaneously detach.

Please note that this description has focuses on the lower density liquid being the drop phase and a higher density liquid being the continuous phase. The Krüss Drop Volume Tensiometer, DVT-10, can be operated either in this configuration or in the opposite configuration, wherein the higher density liquid is the drop phase. This "opposite" configuration is analogous in terms of the Tate's law equation except that the tip is pointed downward into the less dense, continuous phase. The adherence force then acts in the upward direction and the separation force acts in the downward direction.

An examination of Tate's equation shows that, for a given experiment, all values other than the volume of the drop and the interfacial tension are constants. Therefore, by pumping liquid at a fixed flow rate through the tip and detecting the volume of each

drop at its point of detachment, the interfacial tension between virtually any pair of immiscible liquids can be measured. The Krüss Drop Volume Tensiometer DVT-10 operates on this principle. The system employs a precision syringe pump and a specially designed tip which precisely controls droplet formation and eliminates the need for Tate's law correction factors. Drops are grown at various rates on the tip and their detachment from the tip is detected by an infrared LED/photodiode device. Resultant values of interfacial tension are calculated by the DVT-10 (one for each drop produced). Collection of this data using a personal computer with DVT-10 software facilitates data analysis.

The three sets of experiments were done with the PCE/water system. The first set was done with the PCE as the continuous phase, water as the drop phase, and a tungsten carbide tip (0.0254 cm ID opening diameter). The following data was obtained:

<u>Flow Rate</u>	<u>Number of Drops</u>	<u>Relative Standard Deviation</u>	<u>Mean Surface Tension</u>
5.0 ml/hr	5	3.70 %	31.10 mN/m
2.0	10	3.46	25.12
1.0	10	2.73	22.13
0.5	10	2.62	19.14

However, under these conditions the PCE was in contact with a rubber O-ring during the experiment. The literature value for the interfacial tension between pure perchloroethylene and water is approximately 48 mN/m. Therefore, we suspected that the PCE was leaching material from the O-ring during these experiments, and attributed these somewhat low values to that leaching. This data should be discarded.

A second series of experiments was thus performed in the same manner (PCE continuous phase, tungsten carbide tip), but with a Kalrez (a much more resistant rubber) O-ring. The results of this second set of experiments are as follows:

<u>Flow Rate</u>	<u>Number of Drops</u>	<u>Relative Standard Deviation</u>	<u>Mean Surface Tension</u>
5.0 ml/hr	10	2.99 %	46.37 mN/m
2.0	10	2.06	47.64
1.0	10	2.48	45.95
0.5	10	2.00	44.75

We considered this set of experiments to be more reliable (closer to the literature value and less dependent on flow rate). However, we decided that no contact between the PCE phase and any rubber part would be more desirable. Therefore, this data was also discarded.

No contact between the PCE and rubber could be achieved by running the experiments with the aqueous phase as the continuous phase and the perchloroethylene phase as the drop phase. This is the method we used for testing PCE a third time, as well as for all of the drop volume tests on samples C1, C2, C3, and C4. We also found that when using perchloroethylene as the drop phase, a tungsten carbide tip was not appropriate. The perchloroethylene tended to wet the outside of the tip, thus causing us to have an uncontrollable effective tip diameter. Therefore, we switched to an alumina tip of the same diameter (0.0254cm). This eliminated the wetting problem.

The results of drop testing using the alumina tip, using the perchloroethylene phase as drop phase configuration, and assuming that all of the perchloroethylene phases had densities = 1.62g/cm^3 while all of the water phases had densities = 0.998g/cm^3 , are summarized in figure 2. All of these results were obtained at room temperature. The raw data from which figure 2 was constructed is included in the appendix to this report.

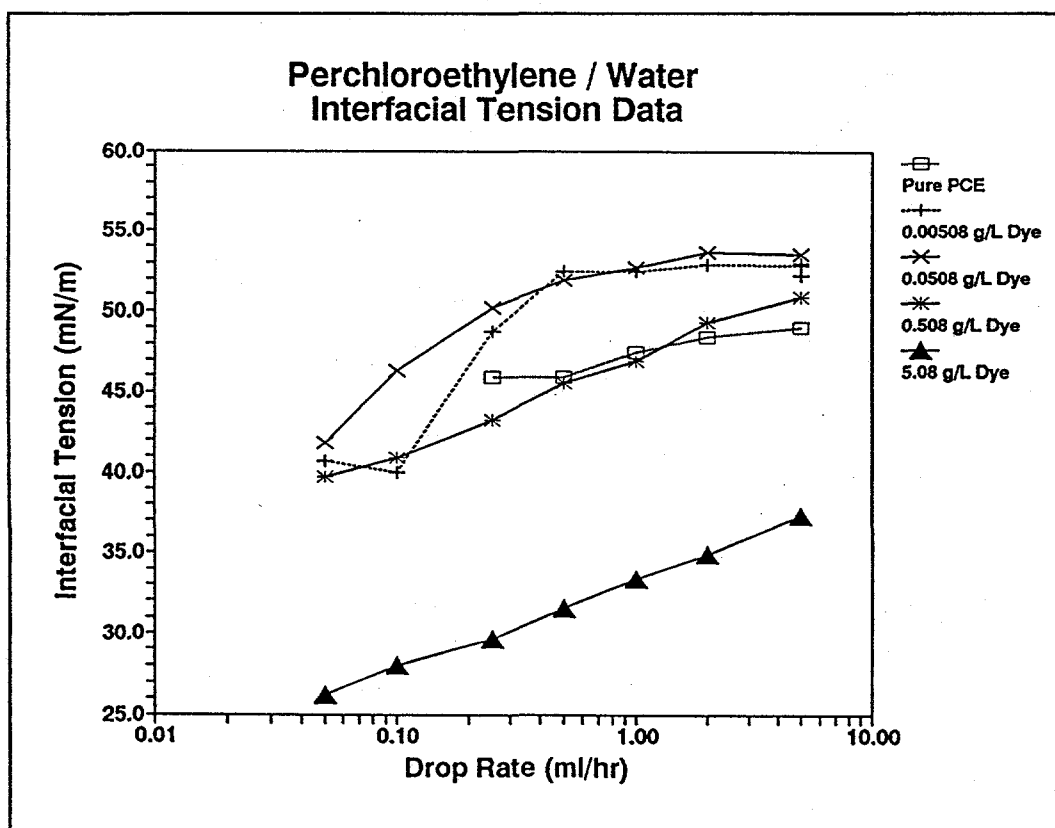


Figure 2

To interpret the results shown in figure 2, consider what dynamic interfacial tension might be telling us about the properties of the dye (solute) that we are studying. Solutes can be either interfacially active or interfacially inactive. Interfacially active solutes are thermodynamically driven to the boundaries of solutions in which they are contained. Surfactants in water are a common example of interfacially active solutes. Figure 3 represents (in highly schematic format) dynamic interfacial tension studies with interfacially active solutes.

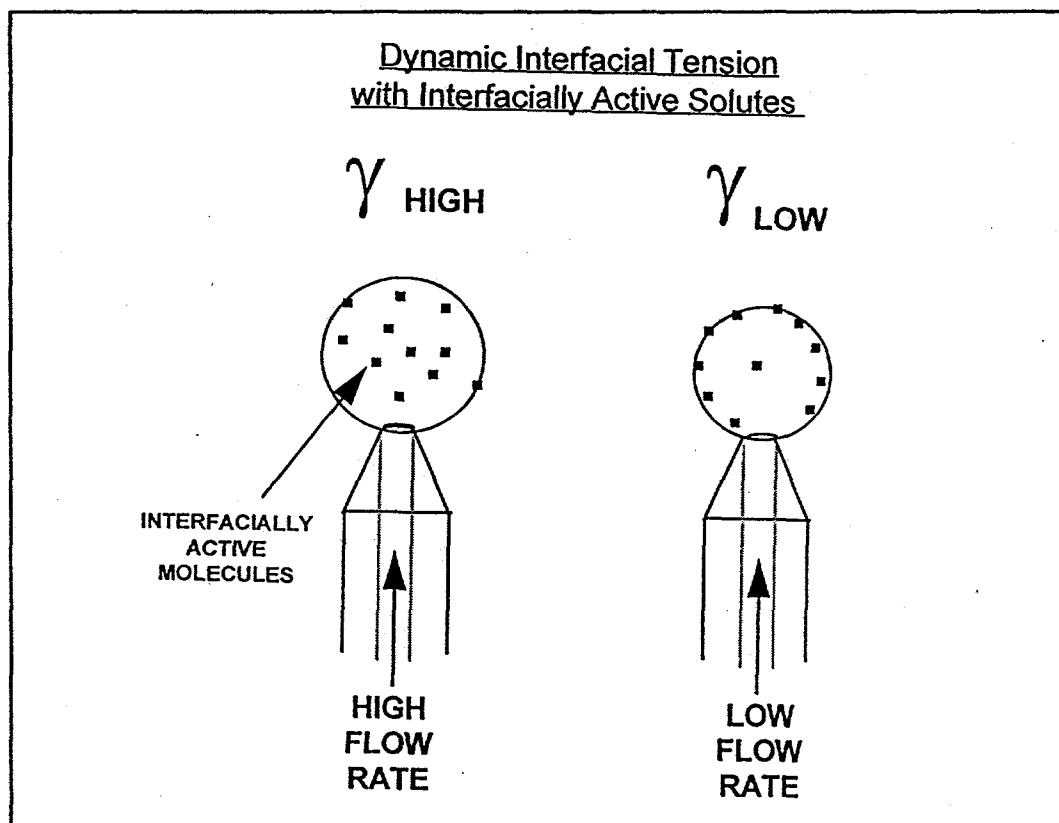


Figure 3

Consider the small black squares in figure 3 to be interfacially active molecules. If a drop is formed rather quickly (at a high flow rate) the active molecules do not have sufficient time to diffuse to and adsorb at the interface substantially. Therefore, the measured interfacial tension is high, relative to what it would be if the drop was formed more slowly. If the drop was formed more slowly (at a low flow rate), the active molecules have more time to adsorb at the interface before the interfacial tension is measured. The measured interfacial tension is thus lower.

Now consider interfacially inactive solutes. In this case, it is more thermodynamically favorable not to have solute molecules at the interface. In other words, thermodynamically inactive molecules increase interfacial tension if they are contained at interfaces. When a drop containing interfacially inactive solute molecules is formed quickly, some of these molecules may (by random chance) be at or near the interface. The interfacial tension between the two liquids being studied may then be even higher in interfacial tension than it would be if the liquids were "pure", due to the presence of the solute. If lower flow rates are studied, time is provided for the inactive solute molecules to diffuse away from the interface and into the bulk of the phase in which they are contained. This decreases interfacial tension. This situation is depicted in figure 4.

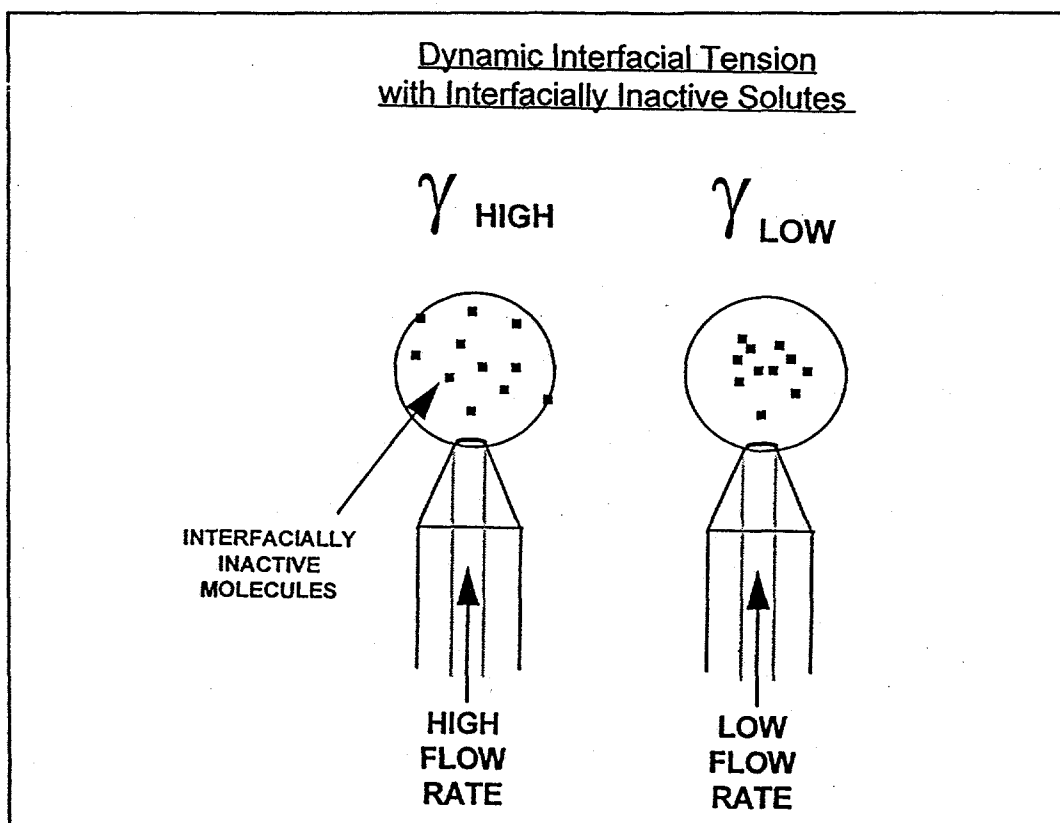


Figure 4

From these explanations two things become evident.

- (1) Solutes (including dyes) can either raise or lower the interfacial tension between two liquids depending on whether they are interfacially active or interfacially inactive.

- (2) It is generally true that, whether or not our solutes are interfacially active or interfacially inactive, interfacial tension will decrease with decreasing drop formation rate.

What does this tell us about the dynamic interfacial tension results that we have in figure 2? It tells us two things mainly.

- (1) Considering the "pure" PCE data, we see a decrease in interfacial tension with decreasing flow rate, the magnitude of which is approximately $\pm 3.0\text{mN/m}$ over the range of flow rates studied. This suggests that there are slight impurities in the PCE.
- (2) The data on the dye solutions suggests that the dye is both interfacially active and interfacially inactive. At low dye concentrations (0.00508 g/L, 0.0508 g/L, and even 0.508g/L) and high drop formation rates the dye increases the interfacial tension between PCE and water, suggesting that the dye is interfacially inactive. This would correlate with the dye being very hydrophobic. Viewing the samples also suggests that this is the case, because the partitioning of the dye between the PCE and the aqueous phase strongly favors the PCE phase. On the other hand, studies at low drop formation rates and higher dye concentrations (5.08g/L) suggest that the dye is interfacially active, since it lowers the interfacial tension between the PCE and the water.

How can this behavior be explained? Three possible explanations come to my mind.

- (1) The dye is not a single molecular species. It is at least a two component species. One component (call it "A") is very hydrophobic and interfacially inactive. It drives the interfacial tension up at high flow rates, because it does not have sufficient time to diffuse away from the developing interface. A second component (call it "B") is interfacially active. It diffuses to developing interfaces (as the drop formation time allows) and decreases interfacial tension.

I could envision this scenario being the result of the dye having been synthesized by a bi-phase or multi-phase technique, using surfactant-like materials as a stabilizing material for the synthesis. The dye product would then be component "A" with an impurity being the surfactant component "B". I could also envision the dye being a collection of isomers, each of which might have different interfacial activities. The purity of your dye might perhaps be explored by HPLC. I'd be interested to know what (if any) data you have on the purity of the dye.

Following the two component scenario a bit further. We can safely assume that component "A" is the more predominate. However, component "B" is strongly driven to replace any component "A" that might be at a developing interface. At dye low concentrations and fast drop formation rates "A" dominates the interface. "B" replaces it as time allows (at lower drop formation times). At higher concentrations (say the 5.08g/L concentration) and fast rates "A" should still dominate the interface, if we could form drops fast enough to see its effect. We have to form drops faster to see the effects of "A" at high dye concentrations because, although the concentration of "B" is only increased proportionately to the concentration of "A" when dye concentration is increased, the amount of available "A" in the bulk of the drop matters less in terms of interfacial tension than does the amount of available "B". In our tests at 5.08g/L we did not explore rates which were fast enough to see the effects of "A". At 0.508g/L we did, but just barely.

- (2) A second scenario, which could explain the behavior of the dye without going to a two component model, is that the dye molecules have a thermodynamically most stable conformation at an interface that is different than their thermodynamically most stable conformation in the bulk. Such things have been reported for surface active polymeric materials. In this scenario the dye molecules at the interface alter their conformation over time, thus explaining the decrease in interfacial tension with decreasing drop formation rate profiles, and the decreasing interfacial tension with increasing concentration profiles. At high flow rates, a portion of the dye molecules are "caught" in a conformation not conducive to being at the developing interface. Interfacial tension is thus high (even higher than for the pure liquids). At low flow rates, the molecules have time to rearrange to provide for a lowering of interfacial tension.

Alternatively, the dye molecules might also change conformations in the bulk as a function of concentration (possibly taking on a more surface active conformation at high concentrations). This is not overly unusual behavior for molecules which contain chromophores. It could be explored by seeing if the UV and/or FTIR spectra for this dye shift based on concentration.

- (3) A third explanation, and the one that I recommend for you to explore first, is that the dye is just interfacially active. It is not inactive, and it does not really increase the interfacial tension between PCE and water. This is what you suspected in the first place, and it does not necessarily mean that the data that we obtained is bad, only that it is misinterpreted.

Remember that the use of Tate's equation requires that values for $\Delta\rho$, r , and g be defined. We have, so far, assumed that the density of each of the dye solutions was 1.62g/cm^3 (and that the density of each aqueous phase was

0.998g/cm³). What if this is a bad assumption?

Using this assumption we obtained 52.24mN/m as the interfacial tension between the 0.00508g/L (C4) solution and water at 5ml/hr. However, what if PCE with this amount of dye in it has a density of 1.58g/cm³ instead of 1.62g/cm³? I don't think that this is totally unreasonable. The correct interfacial tension for the C4/water system would then be:

$$52.24 \frac{1.58-0.998}{1.62-.998} = 48.9 \text{ mN/m}$$

This would be very comparable to the "pure" PCE/water value (obtained using 1.62g/cm³ as the density) of 48.9mN/m.

I think you should determine the correct densities for each of your systems, and possibly correct all of the data for density. This might reveal that the dye only acts as an interfacially active solute, thus making it unnecessary to explore scenarios 1 and 2 above. On the other hand, the interfacial contact angle data (reported below) suggests that scenarios 1 and 2 will need to be considered. It implies that low concentrations of dye really do increase the interfacial tension between PCE/water.

Interfacial contact angle tests

Interfacial contact angle tests were performed using a Krüss Goniometer model G10. For each experiment a drop of perchloroethylene solution was placed on a glass slide which was submerged in water that had been pre-equilibrated with "pure" PCE. The contact angle was measured through the PCE phase as depicted in figure 5 below.

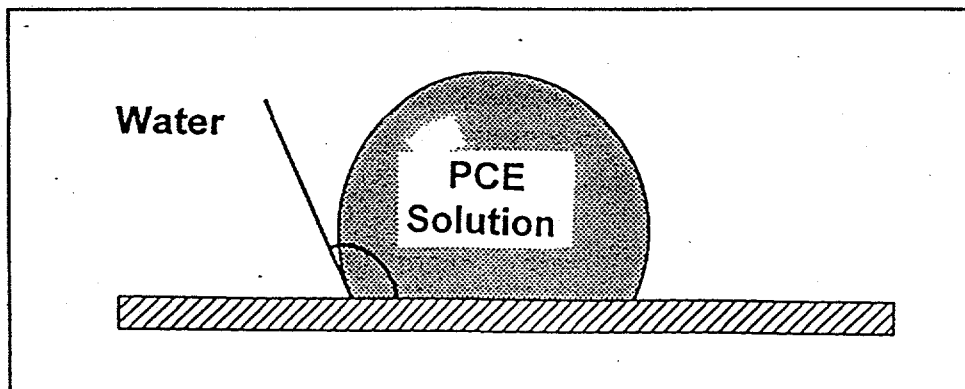


Figure 5

Seven solutions were tested {C1, C2, C3,C4, PCE, X1, and X2}. The contact angle values obtained were:

<u>Solution</u>	<u>Dye Concentration</u>		<u>Contact Angle</u>
PCE	0	g/L	122° ± 3°
C4	0.00508	g/L	139° ± 3°
C3	0.0508	g/L	129° ± 3°
C2	0.508	g/L	133° ± 3°
X1	1.27	g/L	110° ± 3°
X2	1.69	g/L	105° ± 3°
C1	5.08	g/L	87° ± 3°

This data is also plotted in figure 6.

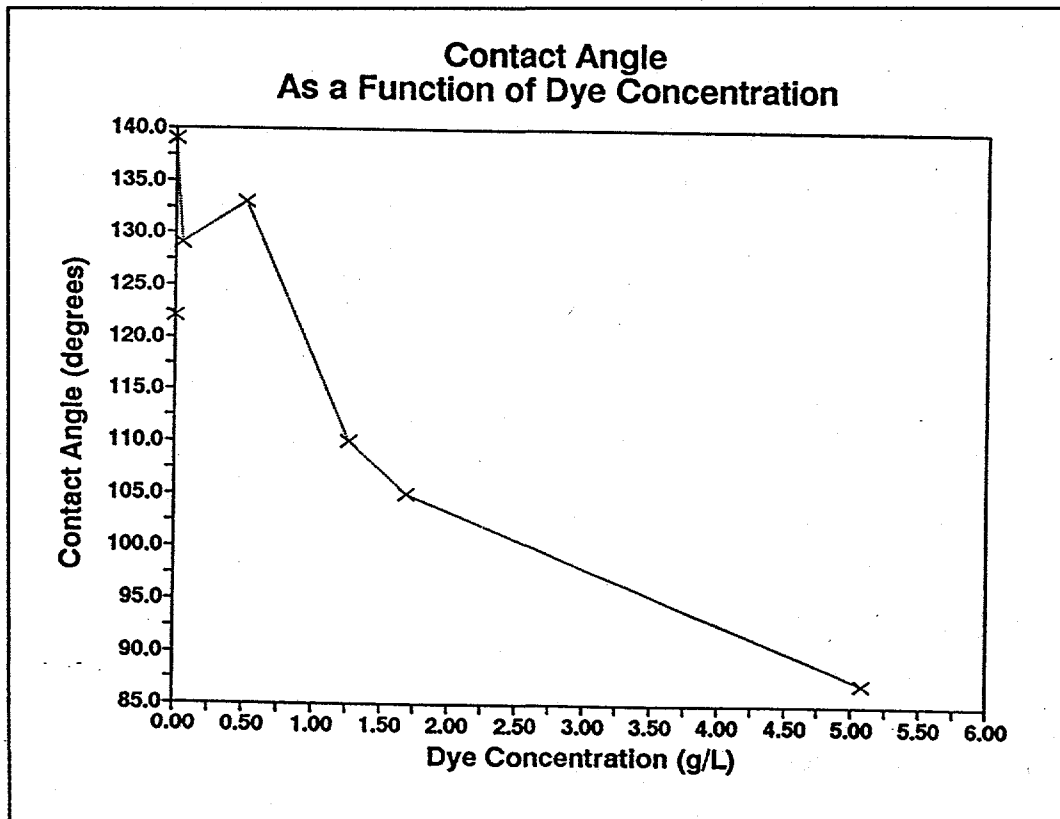


Figure 6

The interfacial contact angle reflects the ability (or lack there of) of the PCE to spontaneously displace water from a glass surface. Angles less than 90° indicate that the displacement is spontaneous. Angles greater than 90° indicate that the displacement will not occur without energy input.

That the interfacial contact angle is greater for low dye concentrations than it is for PCE alone, suggests that the dye is making the PCE less able to wet the glass at low concentrations. At high dye concentrations the PCE/dye solutions become more capable of wetting the glass than the PCE alone is. This is very reminiscent of the drop volume data for these solutions at say 5ml/hr, wherein low concentrations of dye increased interfacial tension while high concentrations of dye decreased it.

Spinning drop data

We also determined the interfacial tensions between four two phase systems containing Dowfax C6L, PCE, and water. The Dowfax concentration was altered throughout the series. For this work a Krüss Spinning Drop Tensiometer SITE04 was used. The principle of spinning drop tensiometry is that if two immiscible liquids are spun in a capillary with the more dense phase being continuous and the less dense phase present as a droplet, then the droplet will become elliptical within the capillary. If this procedure is carried out such that the long radius of the droplet is at least four times the short radius, and the droplet does not touch the capillary walls, then the interfacial tension between the two liquids can be calculated from:

$$\sigma = \frac{r^3 \Delta\rho \omega^2}{4}$$

wherein r = the short radius of the drop, $\Delta\rho$ = the difference in density between the two liquids, and ω = the angular velocity of the spin.

The following data was obtained on the Dowfax systems:

<u>Dowfax Concentration</u>	<u>Spin Velocity (rpm)</u>	<u>Drop Diameter (eyepiece units)</u>	<u>Interfacial Tension (mN/m)</u>
23%	5520	1.25	0.81 mN/m
23%	6922	1.11	0.89 mN/m
23%	3820	1.60	0.81 mN/m
23%	4446	1.42	0.77 mN/m
23%	2499	2.09	0.78 mN/m

9.14%	4445	1.47	0.85 mN/m
9.14%	5335	1.31	0.87 mN/m
9.14%	6935	1.11	0.90 mN/m
9.14%	4580	1.41	0.80 mN/m
9.14%	5556	1.27	0.86 mN/m
4.57%	4544	1.65	1.26 mN/m
4.57%	5635	1.50	1.46 mN/m
4.57%	4773	1.57	1.20 mN/m
4.57%	7038	1.25	1.32 mN/m
4.57%	3521	1.97	1.29 mN/m
1.828%	4426	1.95	1.98 mN/m
1.828%	5010	1.83	2.09 mN/m
1.828%	7123	1.50	2.33 mN/m
1.828%	6289	1.57	2.08 mN/m
1.828%	7766	1.35	2.02 mN/m

In general, the interfacial tension decreases with increasing Dowfax concentration as would be expected.

DuNouy ring method

One other set of interfacial tension experiments which were performed were DuNouy ring tests on the "pure" PCE/water system. For these experiments a Krüss Processor Tensiometer K12 was used. The ring used was constructed of a platinum alloy. Both the push and the pull methods were explored.

We found that it was difficult to tell if the ring was better wetted by water or PCE. We obtained some data from both the push and the pull method, which suggested that the interfacial tension between the two phases was approximately 30mN/m and decreased with time. This data was not well understood. However, it was thought that ring wetting problems existed. The unusually high density difference between the two phases might also have been a contributing factor to the wetting problem.

Reference

1. Tate, T.; *Phil. Mag.*, 27, 176, (1864).

Virginia Weathers
head of ref.
4866

→
<http://www.sc.edu>

Philosophical Magazine
USC- Thomas Cooper Lib. back to 1840

Date Data Collected: November 14, 1995

Experiment Title: pce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 5.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	4.250	4.250	5.900	45.091
2	4.570	8.820	6.350	48.539
3	4.560	13.390	6.330	48.380
4	4.620	18.000	6.410	48.963
5	4.670	22.670	6.490	49.547
6	4.550	27.220	6.320	48.274
7	4.780	32.000	6.640	50.714
8	4.660	36.660	6.470	49.441
9	4.790	41.450	6.650	50.820
10	4.720	46.170	6.560	50.077

Average Drop Volume: 6.413 μ L
Mean Interfacial Tension: 48.985 mN/m
Final Standard Deviation: +/- 1.643 mN/m
Relative Standard Deviation: 3.355 %

12:31:39 PM

11/22/95

PCE into H₂O
5ml/HR

Date Data Collected: November 14, 1995

Experiment Title: pce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 2.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	11.350	11.350	6.310	48.168
2	11.210	22.560	6.230	47.552
3	11.260	33.820	6.260	47.786
4	11.530	45.350	6.410	48.932
5	11.220	56.560	6.230	47.595
6	11.710	68.270	6.500	49.674
7	11.290	79.550	6.270	47.892
8	11.630	91.180	6.460	49.335
9	11.330	102.510	6.290	48.083
10	11.490	114.000	6.380	48.762

Average Drop Volume: 6.333 μ L
Mean Interfacial Tension: 48.378 mN/m
Final Standard Deviation: +/- 0.750 mN/m
Relative Standard Deviation: 1.550 %

12:39:14 PM

11/22/95

PCE into H₂O
2 ml / HR

Date Data Collected: November 14, 1995

Experiment Title: pce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 1.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	22.030	22.030	6.120	46.746
2	23.000	45.030	6.390	48.804
3	21.910	66.940	6.090	46.491
4	22.860	89.800	6.350	48.497
5	22.160	111.950	6.150	47.011
6	22.130	134.080	6.150	46.958
7	22.760	156.850	6.320	48.306
8	22.040	178.890	6.120	46.778
9	22.800	201.690	6.330	48.369
10	21.930	223.610	6.090	46.523

Average Drop Volume: 6.211 μ L
Mean Interfacial Tension: 47.448 mN/m
Final Standard Deviation: +/- 0.923 mN/m
Relative Standard Deviation: 1.945 %

12:40:06 PM

11/22/95

PCE into H₂O

1ml/hr

Date Data Collected: November 14, 1995

Experiment Title: pce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.500 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	43.710	43.710	6.070	46.369
2	41.500	85.200	5.760	44.025
3	42.800	128.000	5.940	45.409
4	43.220	171.230	6.000	45.860
5	42.430	213.660	5.890	45.017
6	43.800	257.460	6.080	46.470
7	43.120	300.570	5.990	45.743
8	43.290	343.860	6.010	45.929
9	44.700	388.560	6.210	47.425
10	43.950	432.520	6.100	46.635

Average Drop Volume: 6.007 μ L
Mean Interfacial Tension: 45.888 mN/m
Final Standard Deviation: +/- 0.941 mN/m
Relative Standard Deviation: 2.051 %

12:40:49 PM

11/22/95

PCE into H₂O
0.5 ml/hr

Date Data Collected: November 14, 1995
Experiment Title: pce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.250 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	85.690	85.690	5.950	45.457
2	85.470	171.160	5.940	45.340
3	85.360	256.520	5.930	45.282
4	86.510	343.030	6.010	45.889
5	86.010	429.030	5.970	45.624
6	87.460	516.490	6.070	46.393
7	86.890	603.380	6.030	46.094
8	86.000	689.370	5.970	45.619
9	87.460	776.830	6.070	46.396
10	88.270	865.110	6.130	46.828

Average Drop Volume: 6.008 μ L
Mean Interfacial Tension: 45.892 mN/m
Final Standard Deviation: +/- 0.520 mN/m
Relative Standard Deviation: 1.133 %

12:41:47 PM

11/22/95

PCE into H₂O
0.25 ml / HR

Date Data Collected: November 14, 1995

Experiment Title: npce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 5.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	5.040	5.040	7.000	53.473
2	4.970	10.010	6.900	52.677
3	4.920	14.930	6.830	52.199
4	5.010	19.940	6.960	53.154
5	4.950	24.890	6.880	52.518
6	5.070	29.960	7.050	53.844
7	5.010	34.970	6.950	53.101
8	5.000	39.970	6.940	53.048

Average Drop Volume: 6.938 μ L
Mean Interfacial Tension: 53.002 mN/m
Final Standard Deviation: +/- 0.528 mN/m
Relative Standard Deviation: 0.996 %

11:16:11 AM

11/22/95

PCE ~~conc~~ $C_4 = 0.00508$ g/L DYE SOLUTION
5ml/HR INTO H₂O

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 5.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	5.110	5.110	7.100	54.215
2	4.760	9.870	6.610	50.502
3	5.100	14.970	7.080	54.109
4	4.780	19.760	6.650	50.767
5	5.020	24.770	6.970	53.207
6	4.820	29.590	6.690	51.085
7	4.930	34.520	6.850	52.305
8	4.860	39.380	6.750	51.563
9	4.840	44.220	6.720	51.351
10	5.020	49.240	6.980	53.313

Average Drop Volume: 6.839 μ L
Mean Interfacial Tension: 52.242 mN/m
Final Standard Deviation: +/- 1.385 mN/m
Relative Standard Deviation: 2.651 %

11:15:32 AM

11/22/95

PCE ~~100~~ $C_A = 0.00508$ g/L DYE SOLUTION
into H₂O
5 ml / HR

Date Data Collected: November 14, 1995

Experiment Title: npce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 2.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	12.380	12.380	6.880	52.539
2	12.450	24.830	6.920	52.836
3	12.540	37.370	6.960	53.197
4	12.380	49.750	6.880	52.539
5	12.600	62.340	7.000	53.451
6	12.440	74.780	6.910	52.794
7	12.500	87.280	6.940	53.048
8	12.550	99.830	6.970	53.239
9	12.260	112.080	6.810	52.008
10	12.660	124.740	7.030	53.706

Average Drop Volume: 6.930 μ L
Mean Interfacial Tension: 52.936 mN/m
Final Standard Deviation: +/- 0.499 mN/m
Relative Standard Deviation: 0.942 %

12:28:25 PM

11/22/95

PCE ~~600~~ $C_4 = 0.00508$ g/L DYE SOLUTION
into H₂O

2 ml/hr

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 1.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	24.860	24.860	6.900	52.740
2	24.650	49.510	6.850	52.305
3	24.620	74.130	6.840	52.252
4	25.360	99.490	7.040	53.812
5	24.170	123.660	6.710	51.287
6	25.070	148.730	6.960	53.197
7	24.410	173.140	6.780	51.786
8	24.750	197.890	6.880	52.518
9	24.510	222.400	6.810	52.008
10	24.730	247.130	6.870	52.475

Average Drop Volume: 6.865 μ L
Mean Interfacial Tension: 52.438 mN/m
Final Standard Deviation: +/- 0.711 mN/m
Relative Standard Deviation: 1.356 %

12:29:12 PM

11/22/95

PCE ~~1000~~ $C_4 = 0.00508$ g/L DYE SOLUTION

into H₂O

1ml/HR

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.500 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	24.860	24.860	6.900	52.740
2	24.650	49.510	6.850	52.305
3	24.620	74.130	6.840	52.252
4	25.360	99.490	7.040	53.812
5	24.170	123.660	6.710	51.287
6	25.070	148.730	6.960	53.197
7	24.410	173.140	6.780	51.786
8	24.750	197.890	6.880	52.518
9	24.510	222.400	6.810	52.008
10	24.730	247.130	6.870	52.475

Average Drop Volume: 6.865 μ L
Mean Interfacial Tension: 52.438 mN/m
Final Standard Deviation: +/- 0.711 mN/m
Relative Standard Deviation: 1.356 %

12:30:15 PM

11/22/95

PCE ~~10~~ $C_A = 0.00508$ g/L DYE SOLUTION

0.5 ml/HR

into H₂O

This data was not correct.
The next page contains the
correct results. 1

Date Data Collected: November 14, 1995

Experiment Title: npce\water

Experimenter: chris

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
 Dispersed Phase Density: 0.998 g/cc
 Orifice Diameter: 0.0254 cm
 Syringe Diameter: 2.3000 cm
 Flow Rate: 0.500 mL/hour
 Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (µL)	Interfacial Tension (mN/m)
1	49.630	49.630	6.920	52.645
2	49.320	98.950	6.850	52.326
3	49.250	148.200	6.840	52.263
4	49.830	198.030	6.920	52.249
5	48.860	246.890	6.930	51.839
6	50.120	297.010	6.960	53.176
7	49.200	346.210	6.830	52.927
8	49.210	395.420	6.830	52.210
9	49.990	445.410	6.940	53.037
10	49.460	494.870	6.870	52.475

Average Drop Volume: 6.889 µL
 Mean Interfacial Tension: 52.515 mN/m
 Final Standard Deviation: +/- 0.402 mN/m
 Relative Standard Deviation: 0.765 %

15:57:48

3/27/97

PCE C4 = 0.00508 g/L DYE SOLUTION
 INTO WATER
 0.5 ml/hr

Correct results for this run
 received by FAX from Krüss USA 3/27/97

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.250 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	93.530	93.530	6.490	49.613
2	91.990	185.520	6.390	48.799
3	91.700	277.220	6.370	48.645
4	89.830	367.050	6.240	47.653
5	91.180	458.230	6.330	48.369
6	90.760	548.980	6.300	48.144
7	92.650	641.640	6.430	49.152
8	90.880	732.520	6.310	48.210
9	93.710	826.220	6.510	49.709
10	92.460	918.680	6.420	49.051

Average Drop Volume: 6.380 μ L
Mean Interfacial Tension: 48.735 mN/m
Final Standard Deviation: +/- 0.661 mN/m
Relative Standard Deviation: 1.357 %

12:30:46 PM

11/22/95

PCE ~~(20)~~ $C_4 = 0.00508$ g/L DYE SOLN.
0.250 ml/HR into H₂O

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.100 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	197.730	197.730	5.490	41.957
2	177.100	374.830	4.920	37.579
3	177.830	552.660	4.940	37.733
4	181.900	734.550	5.050	38.597
5	186.070	920.620	5.170	39.482
6	193.300	1113.920	5.370	41.017
7	194.940	1308.860	5.420	41.366
8	187.380	1496.240	5.210	39.761
9	192.820	1689.060	5.360	40.914
10	197.180	1886.240	5.480	41.840

Average Drop Volume: 5.240 μ L
Mean Interfacial Tension: 40.025 mN/m
Final Standard Deviation: +/- 1.641 mN/m
Relative Standard Deviation: 4.100 %

11:13:41 AM

11/22/95

PCE ~~(0.00508)~~ CA = 0.00508 g/L DYE SOLUTION
into H₂O
0.1 ml/HR

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.050 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	420.830	420.830	5.840	44.648
2	397.080	817.910	5.520	42.129
3	366.560	1184.470	5.090	38.891
4	363.530	1547.990	5.050	38.569
5	368.400	1916.390	5.120	39.086

Average Drop Volume: 5.323 μ L
Mean Interfacial Tension: 40.664 mN/m
Final Standard Deviation: +/- 2.648 mN/m
Relative Standard Deviation: 6.511 %

11:14:36 AM

11/22/95

PCE ~~0.050~~ $C_1 = 0.00508$ g/L DYE SOLUTION
into H₂O
0.05 ml/hr

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 5.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	3.520	3.520	4.880	37.293
2	3.530	7.050	4.900	37.452
3	3.530	10.580	4.900	37.452
4	3.510	14.090	4.880	37.240
5	3.540	17.620	4.910	37.505
6	3.610	21.230	5.010	38.248
7	3.520	24.750	4.900	37.399
8	3.500	28.250	4.850	37.081
9	3.480	31.730	4.830	36.922
10	3.490	35.220	4.850	37.028

Average Drop Volume: 4.891 μ L
Mean Interfacial Tension: 37.362 mN/m
Final Standard Deviation: +/- 0.369 mN/m
Relative Standard Deviation: 0.988 %

10:42:00 AM

11/22/95

PCE ~~100~~ $C_1 = 5.08$ g/L DYE SOLUTION
5 ml/HR into H₂O

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 2.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	8.270	8.270	4.590	35.097
2	8.250	16.520	4.580	34.991
3	8.200	24.720	4.560	34.821
4	8.180	32.900	4.540	34.715
5	8.190	41.090	4.550	34.736
6	8.200	49.290	4.560	34.821
7	8.240	57.530	4.580	34.969
8	8.250	65.780	4.580	35.012
9	8.230	74.020	4.580	34.948
10	8.310	82.330	4.620	35.266

Average Drop Volume: 4.574 μ L
Mean Interfacial Tension: 34.938 mN/m
Final Standard Deviation: +/- 0.170 mN/m
Relative Standard Deviation: 0.487 %

10:40:35 AM 11/22/95

PCE ~~100~~ C₁ = 5.08 g/L DYE
into H₂O
2 ml / HR

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 1.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	15.120	15.120	4.200	32.084
2	15.690	30.810	4.360	33.282
3	15.780	46.590	4.380	33.484
4	15.770	62.360	4.380	33.463
5	15.840	78.190	4.400	33.601
6	15.810	94.000	4.390	33.537
7	15.810	109.810	4.390	33.548
8	15.760	125.570	4.380	33.452
9	15.810	141.380	4.390	33.537
10	15.720	157.090	4.370	33.346

Average Drop Volume: 4.364 μ L
Mean Interfacial Tension: 33.333 mN/m
Final Standard Deviation: +/- 0.450 mN/m
Relative Standard Deviation: 1.349 %

10:39:14 AM

11/22/95

PCE ~~0.0~~ $C_1 = 5.08$ g/L DYE
into H₂O
1 mL/HR

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.500 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	30.090	30.090	4.180	31.919
2	30.080	60.170	4.180	31.914
3	29.620	89.780	4.110	31.420
4	29.690	119.470	4.120	31.500
5	29.780	149.250	4.140	31.595
6	29.930	179.180	4.160	31.749
7	29.990	209.170	4.170	31.818
8	29.560	238.730	4.110	31.362
9	29.410	268.130	4.080	31.198
10	29.030	297.160	4.030	30.800

Average Drop Volume: 4.127 μ L
Mean Interfacial Tension: 31.528 mN/m
Final Standard Deviation: +/- 0.353 mN/m
Relative Standard Deviation: 1.118 %

10:43:57 AM

11/22/95

PCE ~~in~~ $C_1 = 5.08 \text{ g/L}$ DYE SOLUTION
into H_2O
0.5 ml/hr

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.250 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μL)	Interfacial Tension (mN/m)
1	55.940	55.940	3.880	29.672
2	57.010	112.950	3.960	30.243
3	56.750	169.700	3.940	30.105
4	56.270	225.960	3.910	29.848
5	55.680	281.640	3.870	29.537
6	57.320	338.960	3.980	30.405
7	55.620	394.580	3.860	29.505
8	54.380	448.960	3.780	28.848
9	53.960	502.920	3.750	28.625
10	55.910	558.830	3.880	29.659

Average Drop Volume: 3.881 μL
Mean Interfacial Tension: 29.645 mN/m
Final Standard Deviation: +/- 0.567 mN/m
Relative Standard Deviation: 1.913 %

10:45:29 AM

11/22/95

PCE ~~0.25~~ $C_1 = 5.08 \text{ g/L}$ DYE SOLUTION
into H₂O
0.25 ml/HR

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.100 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	132.550	132.550	3.680	28.126
2	126.220	258.770	3.510	26.782
3	131.380	390.140	3.650	27.877
4	135.270	525.410	3.760	28.702
5	132.890	658.300	3.690	28.198
6	133.790	792.080	3.720	28.388

Average Drop Volume: 3.667 μ L
Mean Interfacial Tension: 28.012 mN/m
Final Standard Deviation: +/- 0.663 mN/m
Relative Standard Deviation: 2.366 %

10:47:18 AM

11/22/95

PCE ~~in~~ $C_1 = 5.08$ g/L DYE SOLUTION
into H₂O
0.1 ml/hr

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.050 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	247.120	247.120	3.430	26.218
2	254.180	501.290	3.530	26.967
3	244.480	745.770	3.400	25.938
4	253.660	999.430	3.520	26.912
5	235.170	1234.590	3.270	24.950

Average Drop Volume: 3.429 μ L
Mean Interfacial Tension: 26.197 mN/m
Final Standard Deviation: +/- 0.826 mN/m
Relative Standard Deviation: 3.151 %

10:47:59 AM

11/22/95

PCE ~~0.05~~ $C_1 = 5.08$ g/L DYE SOLUTION
into H₂O
0.05 ml/HR

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 5.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	4.890	4.890	6.790	51.881
2	5.110	9.990	7.090	54.162
3	5.070	15.060	7.030	53.738
4	4.980	20.040	6.920	52.836
5	5.190	25.230	7.210	55.064
6	4.910	30.140	6.810	52.040
7	5.110	35.250	7.100	54.215
8	5.050	40.300	7.010	53.579
9	5.010	45.310	6.960	53.154
10	5.160	50.470	7.170	54.746

Average Drop Volume: 7.009 μ L
Mean Interfacial Tension: 53.542 mN/m
Final Standard Deviation: +/- 1.070 mN/m
Relative Standard Deviation: 1.999 %

11:02:26 AM

11/22/95

PCE ~~3~~ $C_3 = 0.0508$ g/L DYE SOLN.
5ml / HR into H₂O

Date Data Collected: November 14, 1995
Experiment Title: npce\water
Experimenter: chris
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 2.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	12.760	12.760	7.090	54.130
2	12.530	25.280	6.960	53.154
3	12.540	37.820	6.960	53.197
4	12.980	50.800	7.210	55.085
5	12.290	63.090	6.830	52.157
6	12.820	75.900	7.120	54.385
7	12.680	88.580	7.050	53.833
8	12.680	101.270	7.040	53.812
9	12.760	114.030	7.090	54.152
10	12.390	126.420	6.880	52.581

Average Drop Volume: 7.023 μ L
Mean Interfacial Tension: 53.649 mN/m
Final Standard Deviation: +/- 0.880 mN/m
Relative Standard Deviation: 1.640 %

11:03:07 AM

11/22/95

PCE ~~(C₃)~~ C₃ = 0.0508 g/L DYE SOLN
into H₂O
2ml / HR

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 1.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	24.650	24.650	6.850	52.305
2	25.070	49.720	6.960	53.186
3	25.200	74.920	7.000	53.473
4	24.550	99.470	6.820	52.104
5	25.050	124.520	6.960	53.154
6	24.390	148.910	6.770	51.743
7	25.210	174.120	7.000	53.494
8	24.570	198.690	6.830	52.146
9	24.900	223.590	6.920	52.836
10	24.920	248.520	6.920	52.889

Average Drop Volume: 6.903 μ L
Mean Interfacial Tension: 52.733 mN/m
Final Standard Deviation: +/- 0.619 mN/m
Relative Standard Deviation: 1.173 %

11:03:35 AM

11/22/95

PCE ~~(C₃)~~ C₃ = 0.0508 g/L DYE SOLN
into H₂O
1ml/HR

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.500 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μL)	Interfacial Tension (mN/m)
1	48.980	48.980	6.800	51.966
2	47.900	96.880	6.650	50.815
3	50.140	147.020	6.960	53.197
4	48.890	195.910	6.790	51.870
5	48.320	244.230	6.710	51.271
6	49.660	293.890	6.900	52.682
7	48.160	342.050	6.690	51.096
8	49.510	391.560	6.880	52.534
9	47.560	439.120	6.610	50.459
10	50.140	489.270	6.960	53.202

Average Drop Volume: 6.795 μL
Mean Interfacial Tension: 51.909 mN/m
Final Standard Deviation: +/- 0.983 mN/m
Relative Standard Deviation: 1.893 %

11:03:59 AM

11/22/95

PCE ~~3~~ $C_3 = 0.0508 \text{ g/L}$ DYE soln
into H₂O
0.5 ml / HR

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.250 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	97.680	97.680	6.780	51.817
2	92.230	189.910	6.400	48.926
3	97.850	287.770	6.800	51.910
4	91.580	379.350	6.360	48.582
5	97.510	476.860	6.770	51.727
6	91.770	568.630	6.370	48.685
7	97.350	665.980	6.760	51.642
8	91.630	757.620	6.360	48.611
9	96.900	854.520	6.730	51.404
10	92.130	946.650	6.400	48.876

Average Drop Volume: 6.574 μ L
Mean Interfacial Tension: 50.218 mN/m
Final Standard Deviation: +/- 1.571 mN/m
Relative Standard Deviation: 3.129 %

11:04:56 AM

11/22/95

PCE ~~Q22~~ $C_3 = 0.0508$ g/L DYE SOLN
into H₂O
0.250 ml / HR

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.100 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	217.770	217.770	6.050	46.209
2	218.820	436.590	6.080	46.431
3	223.250	659.830	6.200	47.371
4	213.470	873.300	5.930	45.297
5	216.740	1090.040	6.020	45.990

Average Drop Volume: 6.056 μ L
Mean Interfacial Tension: 46.259 mN/m
Final Standard Deviation: +/- 0.753 mN/m
Relative Standard Deviation: 1.627 %

11:05:33 AM

11/22/95

PCE ~~(PCE)~~ $C_3 = 0.0508$ g/L DYE SOLUTION
0.100 ml / HR into H₂O

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.050 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	411.000	411.000	5.710	43.605
2	397.780	808.780	5.520	42.203
3	398.530	1207.310	5.540	42.283
4	372.550	1579.860	5.170	39.526
5	392.320	1972.180	5.450	41.624

Average Drop Volume: 5.478 μ L
Mean Interfacial Tension: 41.848 mN/m
Final Standard Deviation: +/- 1.487 mN/m
Relative Standard Deviation: 3.553 %

11:06:29 AM

11/22/95

PCE ~~0.050~~ $C_3 = 0.0508$ g/L DYE SOLUTION
into H₂O
0.050 ml / HR

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 5.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	4.720	4.720	6.560	50.077
2	4.880	9.600	6.770	51.722
3	4.710	14.310	6.540	49.971
4	4.840	19.150	6.720	51.351
5	4.730	23.880	6.570	50.184
6	4.840	28.720	6.720	51.351
7	4.770	33.490	6.620	50.608
8	4.860	38.350	6.750	51.563
9	4.840	43.190	6.720	51.351
10	4.810	48.000	6.690	51.085

Average Drop Volume: 6.667 μ L
Mean Interfacial Tension: 50.926 mN/m
Final Standard Deviation: +/- 0.657 mN/m
Relative Standard Deviation: 1.291 %

10:48:38 AM

11/22/95

PCE ~~(10%)~~ $C_2 = 0.508$ g/L DYE SOLN.
into H₂O
5ml / HR

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 2.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	11.780	11.780	6.540	49.993
2	11.540	23.320	6.410	48.974
3	11.880	35.200	6.600	50.417
4	11.470	46.680	6.370	48.698
5	12.020	58.690	6.680	50.990
6	11.390	70.080	6.330	48.337
7	11.790	81.870	6.550	50.035
8	11.410	93.280	6.340	48.422
9	11.650	104.930	6.470	49.420
10	11.270	116.200	6.260	47.828

Average Drop Volume: 6.455 μ L
Mean Interfacial Tension: 49.311 mN/m
Final Standard Deviation: +/- 1.026 mN/m
Relative Standard Deviation: 2.080 %

10:51:44 AM

11/22/95

PCE ~~CO2~~ $C_2 = 0.508$ g/L DYE SOLN.
into H₂O
2 ml/HR

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 1.000 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	21.900	21.900	6.080	46.470
2	21.890	43.790	6.080	46.438
3	21.990	65.780	6.110	46.661
4	21.930	87.710	6.090	46.544
5	22.590	110.300	6.270	47.924
6	21.550	131.850	5.990	45.728
7	22.290	154.140	6.190	47.298
8	22.240	176.370	6.180	47.181
9	21.770	198.140	6.050	46.194
10	22.970	221.110	6.380	48.741

Average Drop Volume: 6.142 μ L
Mean Interfacial Tension: 46.918 mN/m
Final Standard Deviation: +/- 0.890 mN/m
Relative Standard Deviation: 1.896 %

10:52:48 AM

11/22/95

PCE : ~~0.508~~ $C_2 = 0.508$ g/L DYE SOLN.
into H₂O
1 ml/HR

Date Data Collected: November 14, 1995

Experiment Title:

Experimenter:

Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.500 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	42.760	42.760	5.940	45.367
2	44.230	86.990	6.140	46.926
3	41.120	128.110	5.710	43.627
4	42.960	171.070	5.970	45.579
5	44.050	215.120	6.120	46.730
6	42.110	257.220	5.850	44.672
7	43.040	300.260	5.980	45.664
8	43.370	343.630	6.020	46.014
9	42.020	385.660	5.840	44.587
10	43.780	429.440	6.080	46.449

Average Drop Volume: 5.964 μ L
Mean Interfacial Tension: 45.561 mN/m
Final Standard Deviation: +/- 1.041 mN/m
Relative Standard Deviation: 2.285 %

10:54:58 AM

11/22/95

PCE ~~is~~ $C_2 = 0.508$ g/L DYE SOLN

0.5 ml / HR

into 150

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.250 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	81.420	81.420	5.650	43.189
2	82.570	163.990	5.730	43.802
3	83.250	247.240	5.780	44.163
4	80.950	328.190	5.620	42.942
5	79.490	407.680	5.520	42.168
6	82.230	489.910	5.710	43.622
7	80.280	570.180	5.570	42.587
8	80.450	650.640	5.590	42.677
9	81.260	731.900	5.640	43.107
10	83.450	815.350	5.800	44.269

Average Drop Volume: 5.662 μ L
Mean Interfacial Tension: 43.253 mN/m
Final Standard Deviation: +/- 0.697 mN/m
Relative Standard Deviation: 1.611 %

10:56:29 AM

11/22/95

PCE ~~1.0~~ $C_2 = 0.508$ g/L DYE SOLUTION
into H₂O
0.25 ~~0.25~~ ml/hr

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.100 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	190.940	190.940	5.300	40.516
2	192.390	383.330	5.340	40.823
3	186.780	570.100	5.190	39.632
4	200.100	770.200	5.560	42.459
5	193.110	963.300	5.360	40.977

Average Drop Volume: 5.352 μ L
Mean Interfacial Tension: 40.881 mN/m
Final Standard Deviation: +/- 1.024 mN/m
Relative Standard Deviation: 2.505 %

10:57:25 AM

11/22/95

PCE ~~in~~ $C_2 = 0.508$ g/L DYE SOLN.
into H₂O
0.1 ml/hr

Date Data Collected: November 14, 1995
Experiment Title:
Experimenter:
Comments:

PARAMETERS

Continuous Phase Density: 1.620 g/cc
Dispersed Phase Density: 0.998 g/cc
Orifice Diameter: 0.0254 cm
Syringe Diameter: 2.3000 cm
Flow Rate: 0.050 mL/hour
Drop Limit: 10

DATA

Drop #	Drop Time (seconds)	Total Time (seconds)	Drop Volume (μ L)	Interfacial Tension (mN/m)
1	391.760	391.760	5.440	41.564
2	383.890	775.650	5.330	40.729
3	365.710	1141.360	5.080	38.800
4	371.080	1512.440	5.150	39.370
5	346.200	1858.630	4.810	36.730
6	387.070	2245.700	5.380	41.066

Average Drop Volume: 5.198 μ L
Mean Interfacial Tension: 39.710 mN/m
Final Standard Deviation: +/- 1.797 mN/m
Relative Standard Deviation: 4.524 %

10:59:38 AM

11/22/95

PCE ~~150~~ $C_2 = 0.508$ g/L DYE SOLN.
0.05 ml/HR into H₂O

Appendix B.

Wilhelmy Plate Interfacial Tension Measurements of M-Area DNAPL

June 1994

7/26/94

Date

MSB - 3D DNAPL phase IFT

DNAPL - Water IFT Wilhemy Plate method Krüss Processor
Tensiometer K12

demonstration 7/26/94 by Lee Gilman of Krüss USA

P/IFT

Equilibrated Water with DNAPL - 9.59 mN/m

Fresh tap water with DNAPL phase -

Plate method - problems with formation of the interface?

lower IFT - range of ^{average} measured values 4.15 to 3.59

Ring-Push Method - 1st try - broke through interface

→ delicate interface

→ Modified rate of push to try to minimize chance of breaking the interface

~~Ring Push~~

Fixed Ring Method

range of values: 2.80 to 1.88 mN/m

Errors Again - The interface broke on one side ~~again~~ this time.

Ring-Push / ~~Ring~~ Hanging ^{Ring} Method (i.e., use weight of the ring to measure the IFT)

ring broke through the interface again

Pull ring up through the interface:

Ring-Pull Method - IFT -

interface broke after a few measurements - range: 7.04 to 6.88 mN/m

Date

7/26/94

Title of Experiment

Interfacial Tension Measurements - Krüss USA Demonstration
by Lee Gilman

The following output is from the Krüss Processor Tensiometer K12.

The data are IFT measurements between very well equilibrated DNAPL from MSB-3D and the ground water in that well. The emulsified phase which separated the two phases was removed prior to the analysis.

KRÜSS PROCESSOR TENSIO METER K12 U4.03

Date : 26.07.94
Time : 20:16:52
Sample : 26079420

Vessel diameter = 6.65 cm
Vessel height = 3.75 cm
Method : 9 (P/IFT)
Measurement interval = 10 s
Max. number of values = 50
Min. standard deviation = 0.08

Temperature = 25.4 °C

Value (mN/m)	Average of 5 val.	Deviation of 5 val.	Time hr:min:ss
9.98			00:02:53
9.88			00:03:05
9.81			00:03:18
9.76			00:03:31
9.71	9.83	0.11	00:03:44
9.68	9.77	0.08	00:03:57

Temperature = 25.5 °C

Value (mN/m)	Average of 5 val.	Deviation of 5 val.	Time hr:min:ss
9.64			00:04:37
9.64			00:04:50
9.64			00:05:03
9.61			00:05:16
9.61	9.63	0.01	00:05:29

Temperature = 25.5 °C

Value (mN/m)	Average of 5 val.	Deviation of 5 val.	Time hr:min:ss
9.59			00:06:02
9.59			00:06:15
9.59			00:06:28
9.59			00:06:40
9.59	9.59	0.00	00:06:53

Temperature = 25.5 °C

Value (mN/m)	Average of 5 val.	Deviation of 5 val.	Time hr:min:ss
9.59			00:07:26
9.59			00:07:39
9.59			00:07:52
9.59			00:08:05
9.61	9.59	0.01	00:08:17

END

The IFT reduced from 9.98 mN/m when the measurements were first started to approximately 9.59 mN/m

We attempted to measure the IFT between the DNAPL phase and clean tap water. We had some problems, however, in that the interface was very fragile and was easily broken by the ring when the du Noüy Ring method was used. We also had rather erratic results due to an irregular wetting perimeter around the plate when we applied the plate panel method.

The results of the measurements are recorded on the following page.

Experimenter

Date

Witness

Date

Appendix C.

Recalculated Drop Volume Interfacial Tension Values

IFT = f(Dye Conc., flow rate)

	A	B	C	D	E	F	G	H	I	J	K
1	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.00000 g/L										
2											
3	Equation:	$IFT = (Vd \cdot \rho L \cdot g) / (\pi \cdot d) = IFT = (Vd \cdot (\rho D - \rho L) \cdot g) / (\pi \cdot d)$									
4	where	IFT = Interfacial Tension (dynes/cm or mN/m)									
5		Vd = the volume of the drop (cm ³)									
6		ρL = the difference in the fluid densities (g/cm ³)									
7		ρD = density of the higher density fluid (g/cm ³)									
8		ρL = density of the lower density fluid (g/cm ³)									
9		g = acceleration of gravity (cm/sec ²)									
10		π = standard mathematical meaning									
11		d = diameter of the tip from which the drop is suspended (cm)									
12											
13		numerical value for d (cm):		0.0254							
14		rhoD (g/cm ³):		1.6153							
15		rhoL (g/cm ³):		0.9962							
16		delrho (g/cm ³):		0.6191							
17		numerical value for (delrho * g) / (pi * d) (1/sec ²):		7603.32038							
18											
19	Dye Concentration (g/L)		0.00000		0.00000		0.00000		0.00000		0.00000
20	PCE Flow Rate (mL/hr.)	5.00	5.00	2.00	2.00	1.00	1.00	0.50	0.50	0.25	0.25
21											
22			Interfacial		Interfacial		Interfacial		Interfacial		Interfacial
23		Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension
24		Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)
25											
26	drop # 1	5.90	44.860	6.31	47.977	6.12	46.532	6.07	46.152	5.95	45.240
27	drop # 2	6.35	48.281	6.23	47.369	6.39	48.585	5.76	43.795	5.94	45.164
28	drop # 3	6.33	48.129	6.26	47.597	6.09	46.304	5.94	45.164	5.93	45.088
29	drop # 4	6.41	48.737	6.41	48.737	6.35	48.281	6	45.620	6.01	45.696
30	drop # 5	6.49	49.346	6.23	47.369	6.15	46.760	5.89	44.784	5.97	45.392
31	drop # 6	6.32	48.053	6.5	49.422	6.15	46.760	6.08	46.228	6.07	46.152
32	drop # 7	6.64	50.486	6.27	47.673	6.32	48.053	5.99	45.544	6.03	45.848
33	drop # 8	6.47	49.193	6.46	49.117	6.12	46.532	6.01	45.696	5.97	45.392
34	drop # 9	6.65	50.562	6.29	47.825	6.33	48.129	6.21	47.217	6.07	46.152
35	drop #10	6.56	49.878	6.38	48.509	6.09	46.304	6.1	46.380	6.13	46.608
36											
37	Mean IFT (mN/m)		48.752		48.159		47.224		45.658		
38	Standard Deviation (mN/m)		1.64		0.74		0.92		0.94		
39	Coefficient of Variation (%)		3.37		1.53		1.94		2.07		1.11
40											
41											
42											
43											
44											

$$\text{IFT} = f(\text{Dye Conc.}, \text{flow rate})$$

	L	M	N	O	P	Q	R	S	T	U	V
1	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.00000 g/L										
2											
3							Summary Data: Dye Concentration = 0.00000 g/L				
4											
5								Mean			
6							PCE Flow	Interfacial	Standard		
7							Rate (mL/hr.)	Tension (mN/m)	Deviation		
8											
9							5.00	48.75	1.64		
10							2.00	48.16	0.74		
11							1.00	47.22	0.92		
12							0.50	45.66	0.94		
13							0.25	45.67	0.51		
14							0.10				
15							0.05				
16											
17											
18											
19											
20											
21											
22											
23											
24											
25											
26											
27											
28											
29											
30											
31											
32											
33											
34											
35											
36											
37											
38											
39											
40											
41											
42											
43											
44											

$$IFT = f(\text{Dye Conc.}, \text{flow rate})$$

	W	X	Y	Z	AA	AB	AC
1	Calculations of Average Interface Age - Dye Concentration = 0.00000 g/L						
2							
3		Average interface age is estimated according to Joos and Rillaerts (1981).					
4		average interface age = 3/7*average drop formation time					
5							
6							
7		age = (7*Sav)/(3*tav)					
8		where					
9		Sav =	Surface area of the average drop				
10		tav =	Average formation time for a drop				
11							
12							
13	Dye Concentration (g/L)		0	0	0	0	0
14							
15	Pumping Rate	Pumping Rate	Average Drop	Average Drop	Average Drop	Average Drop Surface	
16	(mL/hr)	(cm ³ /sec)	Volume (uL)	Radius (cm)	Time (sec)	Area (cm ²)	Average Interface Age (sec)
17							
18	5	0.00138889	6.41	0.11524842	4.61664	0.166909017	1.97856
19	2	0.000555556	6.334	0.11477919	11.4012	0.16555266	4.886228571
20	1	0.000277778	6.211	0.11403136	22.3596	0.163402417	9.582685714
21	0.5	0.000138889	6.005	0.11275647	43.236	0.159769104	18.52971429
22	0.25	6.9444E-05	6.007	0.11276899	86.5008	0.159804576	37.07177143
23	0.1	2.7778E-05					
24	0.05	1.3889E-05					
25							
26							
27							
28							
29							
30							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							
43							
44							

IFT = f(Dye Conc., flow rate)

	A	B	C	D	E	F	G	H	I	J	K
45	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.00508 g/L (C4)										
46											
47	Equation:	$IFT = (Vd \cdot \Delta\rho) / (\pi \cdot d) = IFT = (Vd \cdot (\rho_D - \rho_L) \cdot g) / (\pi \cdot d)$									
48	where	IFT = Interfacial Tension (dynes/cm or mN/m)									
49		Vd = the volume of the drop (cm ³)									
50		$\Delta\rho$ = the difference in the fluid densities (g/cm ³)									
51		ρ_D = density of the higher density fluid (g/cm ³)									
52		ρ_L = density of the lower density fluid (g/cm ³)									
53		g = acceleration of gravity (cm/sec ²)									
54		π = standard mathematical meaning									
55		d = diameter of the tip from which the drop is suspended (cm)									
56											
57		numerical value for d (cm):		0.0254							
58		rhoD (g/cm ³):		1.6150							
59		rhoL (g/cm ³):		0.9962							
60		$\Delta\rho$ (g/cm ³):		0.6188							
61	numerical value for ($\Delta\rho \cdot g$) / ($\pi \cdot d$) (1/sec ²):		7603.32038		Missing Data for one set of 5 mL/hr results						
62											
63	Dye Concentration (g/L)	0.00508		0.00508		0.00508		0.00508		0.00508	
64	PCE Flow Rate (mL/hr.)	5.00	5.00	5.00	5.00	5.00	5.00	2.00	2.00	1.00	1.00
65											
66		Interfacial		Interfacial		Interfacial		Interfacial		Interfacial	
67		Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension
68		Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)
69											
70	drop # 1	7.00	53.223	7.10	53.984		0.000	6.88	52.311	6.90	52.463
71	drop # 2	6.90	52.463	6.61	50.258		0.000	6.92	52.615	6.85	52.083
72	drop # 3	6.83	51.931	7.08	53.832		0.000	6.96	52.919	6.84	52.007
73	drop # 4	6.98	52.919	6.65	50.562		0.000	6.88	52.311	7.04	53.527
74	drop # 5	6.88	52.311	6.97	52.995		0.000	7.00	53.223	6.71	51.018
75	drop # 6	7.05	53.603	6.69	50.866		0.000	6.91	52.539	6.96	52.919
76	drop # 7	6.95	52.843	6.85	52.083		0.000	6.94	52.767	6.78	51.551
77	drop # 8	6.94	52.767	6.75	51.322		0.000	6.97	52.995	6.88	52.311
78	drop # 9			6.72	51.094		0.000	6.81	51.779	6.81	51.779
79	drop #10			6.98	53.071		0.000	7.03	53.451	6.87	52.235
80											
81	Mean IFT (mN/m):	52.758		52.007		0.000		52.691		52.189	
82	Standard Deviation (mN/m):	0.53		1.38		0.00		0.49		0.70	
83	Coefficient of Variation (%):	1.00		2.65		#DIV/0!		0.93		1.34	
84											
85	Combined Results for 5 mL/hr flow rate										
86		Mean IFT (mN/m):		52.340							
87		Standard Deviation (mN/m):		1.13							
88		Coefficient of Variation (%):		2.15							

$$\text{IFT} = f(\text{Dye Conc.}, \text{flow rate})$$

	L	M	N	O	P	Q	R	S	T	U	V			
45	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.00508 g/L (C4)													
46														
47	Summary Data: Dye Concentration = 0.00508 g/L													
48														
49	Mean													
50	PCE Flow Interfacial Standard													
51	Rate (mL/hr.) Tension (mN/m) Deviation													
52														
53	5.00 52.34 1.13													
54	2.00 52.69 0.49													
55	1.00 52.19 0.70													
56	0.50 52.19 0.70													
57	0.25 48.50 0.65													
58	0.10 39.85 1.64													
59	0.05 40.48 2.62													
60														
61														
62														
63	Dye Concentration (g/L)		0.00508			0.00508			0.00508					
64	PCE Flow Rate (mL/hr.)		0.50		0.50		0.25		0.25		0.10	0.10	0.05	0.05
65														
66	Interfacial Interfacial Interfacial Interfacial													
67	Drop Tension Drop Tension Drop Tension Drop Tension													
68	Volume (uL) (mN/m) Volume (uL) (mN/m) Volume (uL) (mN/m) Volume (uL) (mN/m)													
69														
70	drop # 1 6.92 52.615 6.49 49.346 5.49 41.742 5.84 44.403													
71	drop # 2 6.85 52.083 6.39 48.585 4.92 37.408 5.52 41.970													
72	drop # 3 6.84 52.007 6.37 48.433 4.94 37.560 5.09 38.701													
73	drop # 4 6.92 52.615 6.24 47.445 5.05 38.397 5.05 38.397													
74	drop # 5 6.93 52.691 6.33 48.129 5.17 39.309 5.12 38.929													
75	drop # 6 6.96 52.919 6.30 47.901 5.37 40.830													
76	drop # 7 6.83 51.931 6.43 48.889 5.42 41.210													
77	drop # 8 6.83 51.931 6.31 47.977 5.21 39.613													
78	drop # 9 6.94 52.767 6.51 49.498 5.36 40.754													
79	drop #10 6.87 52.235 6.42 48.813 5.48 41.666													
80														
81	Mean IFT (mN/m):		52.379			48.502			39.849			40.480		
82	Standard Deviation (mN/m):		0.38			0.65			1.64			2.62		
83	Coefficient of Variation (%):		0.73			1.35			4.11			6.48		
84														
85														
86														
87														
88														

$$IFT = f(\text{Dye Conc., flow rate})$$

	W	X	Y	Z	AA	AB	AC
45	Calculations of Average Interface Age - Dye Concentration = 0.00508 g/L (C4)						
46							
47		Average interface age is estimated according to Joos and Rillaerts (1981).					
48		average interface age = 3/7*average drop formation time					
49							
50							
51		age = (7*Sav)/(3*tav)					
52		where					
53		Sav =	Surface area of the average drop				
54		tav =	Average formation time for a drop				
55							
56							
57	Dye Concentration (g/L)		0.00508	0.00508	0.00508	0.00508	0.00508
58							
59	Pumping Rate	Pumping Rate	Average Drop	Average Drop	Average Drop	Average Drop Surface	
60	(mL/hr)	(cm ³ /sec)	Volume (uL)	Radius (cm)	Time (sec)	Area (cm ²)	Average Interface Age (sec)
61							
62	5	0.00138889	6.88	0.11800899	4.9564	0.175000797	2.124171429
63	2	0.00055556	6.93	0.11827189	12.474	0.175781412	5.346
64	1	0.00027778	6.86	0.11789523	24.7104	0.17466356	10.59017143
65	0.5	0.00013889	6.89	0.11803819	49.6008	0.175087408	21.25748571
66	0.25	6.9444E-05	6.38	0.11505036	91.8576	0.166335849	39.36754286
67	0.1	2.7778E-05	5.24	0.1077561	188.676	0.145912858	80.86114286
68	0.05	1.3889E-05	5.32	0.10832195	383.328	0.147449336	164.2834286
69							
70							
71							
72							
73							
74							
75							
76							
77							
78							
79							
80							
81							
82							
83							
84							
85							
86							
87							
88							

IFT = f(Dye Conc., flow rate)

	A	B	C	D	E	F	G	H	I	J	K
89	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.0508 g/L (C3)										
90											
91	Equation:	$IFT = (Vd \cdot \Delta\rho \cdot g) / (\pi \cdot d) = IFT = (Vd \cdot (\rho_D - \rho_L) \cdot g) / (\pi \cdot d)$									
92		where IFT = Interfacial Tension (dynes/cm or mN/m)									
93		Vd = the volume of the drop (cm ³)									
94		$\Delta\rho$ = the difference in the fluid densities (g/cm ³)									
95		ρ_D = density of the higher density fluid (g/cm ³)									
96		ρ_L = density of the lower density fluid (g/cm ³)									
97		g = acceleration of gravity (cm/sec ²)									
98		π = standard mathematical meaning									
99		d = diameter of the tip from which the drop is suspended (cm)									
100											
101		numerical value for d (cm):		0.0254							
102		rhoD (g/cm ³):		1.6158							
103		rhoL (g/cm ³):		0.9962							
104		delrho (g/cm ³):		0.6196							
105		numerical value for ($\Delta\rho \cdot g$) / ($\pi \cdot d$) (1/sec ²):		7603.32038							
106											
107	Dye Concentration (g/L)	0.0508		0.0508		0.0508		0.0508		0.0508	
108	PCE Flow Rate (mL/hr.)	5.00	5.00	2.00	2.00	1.00	1.00	0.50	0.50	0.25	0.25
109											
110		Interfacial		Interfacial		Interfacial		Interfacial		Interfacial	
111		Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension
112		Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)
113											
114	drop # 1	6.79	51.627	7.09	53.908	6.85	52.083	6.80	51.703	6.78	51.551
115	drop # 2	7.09	53.908	6.96	52.919	6.96	52.919	6.65	50.562	6.40	48.661
116	drop # 3	7.03	53.451	6.96	52.919	7.00	53.223	6.96	52.919	6.80	51.703
117	drop # 4	6.92	52.615	7.21	54.820	6.82	51.855	6.79	51.627	6.36	48.357
118	drop # 5	7.21	54.820	6.83	51.931	6.96	52.919	6.71	51.018	6.77	51.474
119	drop # 6	6.81	51.779	7.12	54.136	6.77	51.474	6.90	52.463	6.37	48.433
120	drop # 7	7.10	53.984	7.05	53.603	7.00	53.223	6.69	50.866	6.76	51.398
121	drop # 8	7.01	53.299	7.04	53.527	6.83	51.931	6.88	52.311	6.36	48.357
122	drop # 9	6.96	52.919	7.09	53.908	6.92	52.615	6.61	50.258	6.73	51.170
123	drop #10	7.17	54.516	6.88	52.311	6.92	52.615	6.96	52.919	6.40	48.661
124											
125	Mean IFT (mN/m):	53.292		53.398		52.486		51.665		49.977	
126	Standard Deviation (mN/m):	1.07		0.88		0.61		0.97		1.57	
127	Coefficient of Variation (%):	2.01		1.64		1.17		1.88		3.15	
128											
129											
130											
131											
132											

$$IFT = f(\text{Dye Conc.}, \text{flow rate})$$

	L	M	N	O	P	Q	R	S	T	U	V
89	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.0508 g/L (C3)										
90											
91							Summary Data: Dye Concentration = 0.0508 g/L				
92											
93								Mean			
94							PCE Flow	Interfacial	Standard		
95							Rate (mL/hr.)	Tension (mN/m)	Deviation		
96											
97							5.00	53.29	1.07		
98							2.00	53.40	0.88		
99							1.00	52.49	0.61		
100							0.50	51.66	0.97		
101							0.25	49.98	1.57		
102							0.10	46.05	0.75		
103							0.05	41.65	1.50		
104											
105											
106											
107	Dye Concentration (g/L)		0.0508		0.0508						
108	PCE Flow Rate (mL/hr.)		0.10	0.10	0.05	0.05					
109											
110			Interfacial		Interfacial						
111		Drop	Tension	Drop	Tension						
112		Volume (uL)	(mN/m)	Volume (uL)	(mN/m)						
113											
114	drop # 1	6.05	46.000	5.71	43.415						
115	drop # 2	6.08	46.228	5.52	41.970						
116	drop # 3	6.20	47.141	5.54	42.122						
117	drop # 4	5.93	45.088	5.17	39.309						
118	drop # 5	6.02	45.772	5.45	41.438						
119	drop # 6										
120	drop # 7										
121	drop # 8										
122	drop # 9										
123	drop #10										
124											
125	Mean IFT (mN/m):		46.046		41.651						
126	Standard Deviation (mN/m):		0.75		1.50						
127	Coefficient of Variation (%):		1.62		3.59						
128											
129											
130											
131											
132											

IFT = f(Dye Conc., flow rate)

	W	X	Y	Z	AA	AB	AC
89	Calculations of Average Interface Age - Dye Concentration = 0.0508 g/L (C3)						
90							
91	Average interface age is estimated according to Joos and Pillaerts (1981).						
92	average interface age = 3/7*average drop formation time						
93							
94							
95	age = (7*Sav)/(3*tav)						
96	where						
97		Sav =	Surface area of the average drop				
98		tav =	Average formation time for a drop				
99							
100							
101	Dye Concentration (g/L)		0.0508	0.0508	0.0508	0.0508	0.0508
102							
103	Pumping Rate	Pumping Rate	Average Drop	Average Drop	Average Drop	Average Drop Surface	
104	(mL/hr)	(cm ³ /sec)	Volume (uL)	Radius (cm)	Time (sec)	Area (cm ²)	Average Interface Age (sec)
105							
106	5	0.00138889	7.01	0.11871962	5.04648	0.177114791	2.162777143
107	2	0.00055556	7.02	0.11879861	12.6414	0.177350562	5.417742857
108	1	0.00027778	6.90	0.11811809	24.8508	0.175324539	10.65034286
109	0.5	0.00013889	6.80	0.11749885	48.924	0.173491059	20.96742857
110	0.25	6.9444E-05	6.57	0.11620505	94.6512	0.169691418	40.5648
111	0.1	2.7778E-05	6.06	0.11307478	218.016	0.160672433	93.43542857
112	0.05	1.3889E-05	5.48	0.10935647	394.416	0.150279178	169.0354286
113							
114							
115							
116							
117							
118							
119							
120							
121							
122							
123							
124							
125							
126							
127							
128							
129							
130							
131							
132							

$$IFT = f(\text{Dye Conc.}, \text{flow rate})$$

	A	B	C	D	E	F	G	H	I	J	K
133	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.508 g/L (C2)										
134											
135	Equation:	$IFT = (Vd \cdot \Delta\rho \cdot g) / (\pi \cdot d) = IFT = (Vd \cdot (\rho_D - \rho_L) \cdot g) / (\pi \cdot d)$									
136	where	IFT = Interfacial Tension (dynes/cm or mN/m)									
137		Vd = the volume of the drop (cm ³)									
138		$\Delta\rho$ = the difference in the fluid densities (g/cm ³)									
139		ρ_D = density of the higher density fluid (g/cm ³)									
140		ρ_L = density of the lower density fluid (g/cm ³)									
141		g = acceleration of gravity (cm/sec ²)									
142		π = standard mathematical meaning									
143		d = diameter of the tip from which the drop is suspended (cm)									
144											
145		numerical value for d (cm):	0.0254								
146		ρ_D (g/cm ³):	1.6147								
147		ρ_L (g/cm ³):	0.9962								
148		$\Delta\rho$ (g/cm ³):	0.6185								
149		numerical value for $(\Delta\rho \cdot g) / (\pi \cdot d)$ (1/sec ²):	7603.32038								
150											
151	Dye Concentration (g/L)		0.508		0.508		0.508		0.508		0.508
152	PCE Flow Rate (mL/hr.)	5.00	5.00	2.00	2.00	1.00	1.00	0.50	0.50	0.25	0.25
153											
154		Interfacial		Interfacial		Interfacial		Interfacial		Interfacial	
155		Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension
156		Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)
157											
158	drop # 1	6.56	49.878	6.54	49.726	6.08	46.228	5.94	45.164	5.65	42.959
159	drop # 2	6.77	51.474	6.41	48.737	6.08	46.228	6.14	46.684	5.73	43.567
160	drop # 3	6.54	49.726	6.60	50.182	6.11	46.456	5.71	43.415	5.78	43.947
161	drop # 4	6.72	51.094	6.37	48.433	6.09	46.304	5.97	45.392	5.62	42.731
162	drop # 5	6.57	49.954	6.68	50.790	6.27	47.673	6.12	46.532	5.52	41.970
163	drop # 6	6.72	51.094	6.33	48.129	5.99	45.544	5.85	44.479	5.71	43.415
164	drop # 7	6.62	50.334	6.55	49.802	6.19	47.065	5.98	45.468	5.57	42.350
165	drop # 8	6.75	51.322	6.34	48.205	6.18	46.989	6.02	45.772	5.59	42.503
166	drop # 9	6.72	51.094	6.47	49.193	6.05	46.000	5.84	44.403	5.64	42.883
167	drop #10	6.69	50.866	6.26	47.597	6.38	48.509	6.08	46.228	5.80	44.099
168											
169	Mean IFT (mN/m):		50.684		49.079		46.700		45.354		43.042
170	Standard Deviation (mN/m):		0.65		1.03		0.88		1.03		0.70
171	Coefficient of Variation (%):		1.28		2.09		1.88		2.27		1.62
172											
173											
174											
175											
176											

$$IFT = f(\text{Dye Conc.}, \text{flow rate})$$

	L	M	N	O	P	Q	R	S	T	U	V
133	Interfacial Tension by Drop Volume Method - Dye Concentration = 0.508 g/L (C2)										
134											
135							Summary Data: Dye Concentration = 0.508 g/L				
136											
137								Mean			
138							PCE Flow	Interfacial	Standard		
139							Rate (mL/hr.)	Tension (mN/m)	Deviation		
140											
141							5.00	50.68	0.65		
142							2.00	49.08	1.03		
143							1.00	46.70	0.88		
144							0.50	45.35	1.03		
145							0.25	43.04	0.70		
146							0.10	40.68	1.02		
147							0.05	39.52	1.79		
148											
149											
150											
151	Dye Concentration (g/L)		0.508		0.508						
152	PCE Flow Rate (mL/hr.)		0.10	0.10	0.05	0.05					
153											
154			Interfacial		Interfacial						
155		Drop	Tension	Drop	Tension						
156		Volume (uL)	(mN/m)	Volume (uL)	(mN/m)						
157											
158	drop # 1	5.30	40.298	5.44	41.362						
159	drop # 2	5.34	40.602	5.33	40.526						
160	drop # 3	5.19	39.461	5.08	38.625						
161	drop # 4	5.56	42.274	5.15	39.157						
162	drop # 5	5.36	40.754	4.81	36.572						
163	drop # 6			5.38	40.906						
164	drop # 7										
165	drop # 8										
166	drop # 9										
167	drop #10										
168											
169	Mean IFT (mN/m):		40.678		39.525						
170	Standard Deviation (mN/m):		1.02		1.79						
171	Coefficient of Variation (%):		2.51		4.52						
172											
173											
174											
175											
176											

$$IFT = f(\text{Dye Conc.}, \text{flow rate})$$

	W	X	Y	Z	AA	AB	AC
133	Calculations of Average Interface Age - Dye Concentration = 0.508 g/L (C2)						
134							
135		Average interface age is estimated according to Joos and Rillaerts (1981).					
136		average interface age = 3/7*average drop formation time					
137							
138							
139		age = (7*Sav)/(3*tav)					
140		where					
141		Sav =	Surface area of the average drop				
142		tav =	Average formation time for a drop				
143							
144							
145	Dye Concentration (g/L)		0.508	0.508	0.508	0.508	0.508
146							
147	Pumping Rate	Pumping Rate	Average Drop	Average Drop	Average Drop	Average Drop Surface	
148	(mL/hr)	(cm ³ /sec)	Volume (uL)	Radius (cm)	Time (sec)	Area (cm ²)	Average Interface Age (sec)
149							
150	5	0.00138889	6.67	0.11675054	4.79952	0.171288286	2.056937143
151	2	0.00055556	6.46	0.11550547	11.619	0.1676544	4.979571429
152	1	0.00027778	6.14	0.11360752	22.1112	0.162189972	9.476228571
153	0.5	0.00013889	5.97	0.11250555	42.948	0.15905882	18.40628571
154	0.25	6.9444E-05	5.66	0.11056089	81.5184	0.153607667	34.93645714
155	0.1	2.7778E-05	5.35	0.108498	192.6	0.147928997	82.54285714
156	0.05	1.3889E-05	5.20	0.10746289	374.28	0.145119868	160.4057143
157							
158							
159							
160							
161							
162							
163							
164							
165							
166							
167							
168							
169							
170							
171							
172							
173							
174							
175							
176							

IFT = f(Dye Conc., flow rate)

	A	B	C	D	E	F	G	H	I	J	K
177	Interfacial Tension by Drop Volume Method - Dye Concentration = 5.08 g/L (C1)										
178											
179	Equation: $IFT = (Vd \cdot \text{delrho} \cdot g) / (\text{Pi} \cdot d) = IFT = (Vd \cdot (\text{rhoD} - \text{rhoL}) \cdot g) / (\text{Pi} \cdot d)$										
180	where IFT = Interfacial Tension (dynes/cm or mN/m)										
181	Vd = the volume of the drop (cm**3)										
182	delrho = the difference in the fluid densities (g/cm**3)										
183	rhoD = density of the higher density fluid (g/cm**3)										
184	rhoL = density of the lower density fluid (g/cm**3)										
185	g = acceleration of gravity (cm/sec**2)										
186	Pi = standard mathematical meaning										
187	d = diameter of the tip from which the drop is suspended (cm)										
188											
189	numerical value for d (cm): 0.0254										
190	rhoD (g/cm**3): 1.6141										
191	rhoL (g/cm**3): 0.9962										
192	delrho (g/cm**3): 0.6179										
193	numerical value for (delrho*g) / (Pi*d) (1/sec**2): 7603.32038										
194											
195	Dye Concentration (g/L)	5.08		5.08		5.08		5.08		5.08	
196	PCE Flow Rate (mL/hr.)	5.00	5.00	2.00	2.00	1.00	1.00	0.50	0.50	0.25	0.25
197											
198	Interfacial		Interfacial		Interfacial		Interfacial		Interfacial		Interfacial
199	Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension	Drop	Tension	
200	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	Volume (uL)	(mN/m)	
201											
202	drop # 1	4.88	37.104	4.59	34.899	4.20	31.934	4.18	31.782	3.88	29.501
203	drop # 2	4.90	37.256	4.58	34.823	4.36	33.150	4.18	31.782	3.96	30.109
204	drop # 3	4.90	37.256	4.56	34.671	4.38	33.303	4.11	31.250	3.94	29.957
205	drop # 4	4.88	37.104	4.54	34.519	4.38	33.303	4.12	31.326	3.91	29.729
206	drop # 5	4.91	37.332	4.55	34.595	4.40	33.455	4.14	31.478	3.87	29.425
207	drop # 6	5.01	38.093	4.56	34.671	4.39	33.379	4.16	31.630	3.98	30.261
208	drop # 7	4.90	37.256	4.58	34.823	4.39	33.379	4.17	31.706	3.86	29.349
209	drop # 8	4.85	36.876	4.58	34.823	4.38	33.303	4.11	31.250	3.78	28.741
210	drop # 9	4.83	36.724	4.58	34.823	4.39	33.379	4.08	31.022	3.75	28.512
211	drop #10	4.85	36.876	4.62	35.127	4.37	33.227	4.03	30.641	3.88	29.501
212											
213	Mean IFT (mN/m):	37.188		34.778		33.181		31.387		29.508	
214	Standard Deviation (mN/m):	0.38		0.17		0.45		0.37		0.56	
215	Coefficient of Variation (%):	1.01		0.50		1.35		1.17		1.89	
216											
217											
218											
219											
220											

$$IFT = f(\text{Dye Conc.}, \text{flow rate})$$

	L	M	N	O	P	Q	R	S	T	U	V
177	Interfacial Tension by Drop Volume Method - Dye Concentration = 5.08 g/L (C1)										
178											
179	Summary Data: Dye Concentration = 5.08 g/L										
180											
181	Mean										
182	PCE Flow										
183	Rate (mL/hr.)										
184	Interfacial Tension (mN/m)										
185	Standard Deviation										
186	5.00										
187	2.00										
188	1.00										
189	0.50										
190	0.25										
191	0.10										
192	0.05										
193											
194											
195	Dye Concentration (g/L)		5.08		5.08						
196	PCE Flow Rate (mL/hr.)		0.10		0.05						
197											
198											
199											
200											
201											
202											
203											
204											
205											
206											
207											
208											
209											
210											
211											
212											
213	Mean IFT (mN/m):		27.892		26.079						
214	Standard Deviation (mN/m):		0.65		0.80						
215	Coefficient of Variation (%):		2.35		3.08						
216											
217											
218											
219											
220											

$$IFT = f(\text{Dye Conc., flow rate})$$

	W	X	Y	Z	AA	AB	AC
177	Calculations of Average Interface Age - Dye Concentration = 5.08 g/L (C1)						
178							
179	Average interface age is estimated according to Joos and Pillaerts (1981).						
180	average interface age = 3/7*average drop formation time						
181							
182							
183	age = (7*Sav)/(3*tav)						
184	where						
185	Sav =		Surface area of the average drop				
186	tav =		Average formation time for a drop				
187							
188							
189	Dye Concentration (g/L)		5.08	5.08	5.08	5.08	5.08
190							
191	Pumping Rate	Pumping Rate	Average Drop	Average Drop	Average Drop	Average Drop Surface	
192	(mL/hr)	(cm ³ /sec)	Volume (uL)	Radius (cm)	Time (sec)	Area (cm ²)	Average Interface Age (sec)
193							
194	5	0.00138889	4.89	0.10530193	3.52152	0.139342169	1.509222857
195	2	0.00055556	4.57	0.10297596	8.2332	0.133254402	3.528514286
196	1	0.00027778	4.36	0.10137527	15.7104	0.129143916	6.733028571
197	0.5	0.00013889	4.13	0.09951389	29.7216	0.124444942	12.73782857
198	0.25	6.9444E-05	3.88	0.09748812	55.8864	0.119429942	23.95131429
199	0.1	2.7778E-05	3.67	0.09567388	132.06	0.115026168	56.59714286
200	0.05	1.3889E-05	3.43	0.09355532	246.96	0.109988397	105.84
201							
202							
203							
204							
205							
206							
207							
208							
209							
210							
211							
212							
213							
214							
215							
216							
217							
218							
219							
220							