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DYNAMIC SURFACE TENSION MEASUREMENTS AND THEIR USE IN PREDICTION OF WETTING ABILITY

by

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INTRODUCTION

As a member of the staffs of the Home Economics Divisions at Cornell University and Iowa State College the author has been interested in textile laundry for a number of years. Textile laundry furnishes a variety of problems of physicochemical character, especially of surface chemical character, few of which have been investigated from a fundamental point of view. The present work was undertaken to obtain a better understanding of one of the most pressing of these problems, namely, the kinetic mechanism of the action of surface active agents in depressing boundary tensions and accelerating wetting of fabrics.

The cleaning of textile fabrics can be divided into three parts: wetting, soil removal, and soil suspension (49). The cleaning process involves both kinetic and equilibrium considerations. The penetration of cleaning solution into the fabric requires a kinetic treatment; soil removal has both kinetic and equilibrium aspects, but soil suspension involves only equilibrium considerations. Each of these processes is dependent on the surface active agent used.

Fischer and Gans (24) define a surface active agent as a compound which in relatively small amounts greatly modifies the physical properties of a heterogeneous system by adsorption at the surface. The adsorption of such a compound at the surface of a liquid brings about a large reduction in the surface tension of the solvent. Surface active agents can be divided into classes by means of the functions they perform, that is, whether they are primarily wetting agents, detergents, or dispersing and emulsifying agents.

Schwartz and Perry (48) explain the great reduction in the surface tension of surface active agents very well. A pure liquid can decrease its free surface energy only by diminishing its surface area. In addition a solution may do so by concentrating in the surface the molecular species with the smaller free surface energy. Surface tension or surface free energy results from unbalanced forces at the surface. Lateral forces of attraction on surface molecules cancel each other. However, forces which pull a surface molecule into the interior are not offset by equivalent attraction in the opposite direction. No two species of molecules are likely to have equal force fields; thus, in a solution the species which has the higher force of attraction will leave the surface at a higher rate than would be predicted from the relative numbers present. As this movement continues, the molecules with the smaller force fields are concentrated at the surface. Thermal agitation acts to prevent the surface from becoming completely bare of molecules with the higher attractive forces.

Molecules or ions which are surface active are often composed of both hydrophilic and hydrophobic groups (43). In the surface of an aqueous solution these molecules or ions are oriented with the hydrophilic part in the water and the hydrophobic part in air. This orientation is caused by the greater attraction between water and the hydrophilic part than between water and the hydrophobic group. One would expect adsorption at a solution-fiber interface to resemble that at the solution-air interface. Work done by others supports this idea.

Bartell and co-workers (7, 8a, 9) showed that interfacial tensions at the interfaces formed between a series of organic liquids and water were related to the interfacial tensions between the same organic liquids and polar solids. Comparison of work by Ward and Tordai (58) on aliphatic alcohols and acids at aqueous solution-air interfaces with work of Hansen and Craig (29) on the adsorption of the same organic compounds from aqueous solutions on carbon black also indicates similar behavior at solution-air and solution-carbon interfaces. From this one would expect information on the solution-air interface to be helpful in understanding the adsorption at the solution-fiber interface.

The energy changes involved in the various types of wetting are as follows (37):

Adhesional $-\Delta F = \gamma_S - \gamma_{SL} + \gamma_L$

Spreading $-\Delta F = \gamma_S - \gamma_{SL} - \gamma_L$

Immersional $-\Delta F = \gamma_S - \gamma_{SL}$

The symbols have the following meanings:

γ_S is the surface tension of a solid

γ_{SL} is the solid-liquid interfacial tension

γ_L is the surface tension of a liquid

In adhesional wetting a solid-air and a liquid-air interface are replaced by a solid-liquid boundary. The free energy of adhesional wetting will be more negative the lower the solid-liquid interfacial tension and the larger the surface tensions of the liquid and solid.

As spreading wetting takes place, the solid surface is covered by a film of liquid so that during wetting the solid-air boundary disappears and solid-liquid and liquid-air interfaces are formed. The free energy of spreading wetting is therefore more negative when both the surface tension of the liquid and the interfacial tension are small.

If the wetting takes place by immersion, the liquid surface tension has no effect on the wetting, but a low interfacial tension promotes wetting.

The first two types of wetting, adhesional and spreading, depend upon the liquid surface tension but the wetting free energy changes are affected in opposite directions by a decrease in this tension. In spreading wetting such a decrease lowers (makes more negative) the wetting free energy.

Fowkes (26) showed that although smooth walled capillaries are wetted by immersion, the process which controls the wetting of cotton fibers is spreading wetting. He says that penetration of solution into a bundle of yarns is from the side of the thread in a direction perpendicular to the length of the fibers and that after entry into the yarn the solution travels parallel to the fibers. Thus the wetting of fabrics would involve both surface and interfacial tensions and the wetting free energy change would be made more negative by decreasing both of these quantities.

As the word "wetting" has been used in the literature, it has had two meanings, one involving free energy changes and the other kinetics. This is unfortunate as it has led to much misunderstanding. Other authors, for example, Bartholeme and Schafer (10), have appeared surprised that the surface active agents which cause the fastest penetration of fabric by liquid are not always the ones with the lowest surface tension. Apparently they do not comprehend that the surface tension as usually measured and the free energy relations apply to equilibrium conditions, whereas the wetting to which they refer is a rate of wetting, a matter of kinetics.

In this work the word "wetting" will be reserved for the wetting under equilibrium conditions and "rate of wetting" will be used in the kinetics problem. With this clarification of meaning it is easily understood why equilibrium surface tension cannot be used to predict rate of wetting. On the other hand, since rate of lowering of surface tension and rate of wetting are both dependent on the rate of adsorption of surface active molecules at an interface, it is reasonable to expect that the rate of wetting of fabric and the rate of lowering of surface tension may be related.

When the surface tensions of fresh surfaces of detergent solutions in laundry concentration ranges are measured by ordinary methods, the values obtained are very nearly the equilibrium values. Apparently the adsorption takes place very rapidly, that is, within a very few seconds. In lower concentrations the surface tension falls more slowly so that common methods can be used to give surface tensions at different times. However, two difficulties appear. The less concentrated solutions are not of as much interest in the problem of wetting and, when the common methods of measuring surface tension are used, it is impossible to determine the exact age of the surface.

Lord Rayleigh (40) described a method which can be used to determine surface tensions of very young surfaces of liquids which also permits estimation of surface ages. The method involves measurements on a stream of liquid issuing from a non-circular orifice. Although the method has many advantages for use in studying the rate of surface tension depression, the method of calculation used by others does not give accurate values for the surface tension near the orifice. Unfortunately, this is the region which is of greatest interest in this case. The error in calculation enters because the theory calls for a uniform velocity over the cross section of the jet, whereas in reality the surface and bulk velocities may be quite different, especially near the orifice.

Two methods are commonly accepted for determining rate of wetting; skein (23a) and canvas disc (50) wetting tests. When these tests are performed under the same conditions, comparisons can be made of the wetting rate of solutions. However, the tests give no insight into the mechanism of wetting and they do not allow one to predict the wetting rate of an agent from its other properties. A more fundamental, less empirical measure which correlates with rate of wetting would be of great value in selecting wetting agents and in producing molecules tailor-made for desirable equilibrium or kinetic wetting properties.

The purposes of the present study were as follows:

1. To refine the vibrating jet method for measuring surface tensions, adapting it for use with non-constant velocity profiles, so that accurate boundary tensions can be determined at accurately known times for very young surfaces.
2. To determine the dependence of surface tensions of aqueous detergent solutions on time and concentration for young surfaces, and to propose a mechanism to explain the observed dependence.

3. To determine the effect of detergent concentration and type on fabric sinking times and to propose a mechanism to explain the observed dependence.
4. To relate, if possible, the effect of detergents on the fabric sinking times to their effect on the rate of surface tension depression.

REVIEW OF LITERATURE

Surface Active Agents

Surface active agents, even in dilute solutions, greatly alter the surface tension of the liquids in which they are dissolved. The change is always a decrease rather than an increase. Molecules which exhibit surface activity in aqueous solution are composed of a non-polar, hydrophobic part and a polar, hydrophilic part (48, p. 5). Common hydrophobic groups are linear hydrocarbon chains, benzene rings, or benzene rings to which alkyl groups have been attached. Among the polar groups are the carboxyl, sulfate and the sulfonate radicals and the ether and amide linkages (48, p. 15).

Surface active agents are often classed according to their use; wetting agents, detergents, emulsifying agents, dispersing agents, and others (48, p. 11). A single compound might be used for more than one purpose as there is much overlapping of the functions (a fact rarely appreciated by the user).

Fischer and Gans (24) say that a variety of terms have been associated with the subject of surface active agents. "Wetting agent" is the term used to indicate improved spreading of a solution over an initially repellent surface. A penetrating agent increases the degree or the speed of passage of liquid into a porous solid. If the agent is used for cleaning or soil removal, it is called a detergent. An emulsifying agent is one which stabilizes the dispersion of one liquid in another even though the two are immiscible.

Another method of classification divides the compounds into anionic, cationic and nonionic agents (48, p. 9). The anionic group is most common and best known, soap itself being the classic example. As the name implies it is the anion in this class which is surface active and the cation has little effect on the activity. In contrast, the cationic agents are compounds containing a cation which is composed of both hydrophobic and hydrophilic groups. In the nonionic compounds the solubilizing group is often made up of a number of oxygen, nitrogen, or sulfur atoms.

When certain properties of solutions of surface active agents are studied over a range of concentrations, discontinuities in the relationship of the property to the concentration are observed. McBain (34) first proposed the formation of aggregates of molecules at the concentration where the discontinuity is observed. The name micelle is given to the aggregate and the lowest concentration at which micelles form is called the critical micelle concentration. Adsorption at the surface occurs above and below the critical micelle concentration, but in either case it is only the single ions or molecules which are adsorbed (48, p. 289).

It has been suggested (19) that molecules which show much branching do not form micelles as readily as less branched or straight chain molecules. In other words, branching increases the critical micelle concentration. In the concentration range where micelles are present, the concentration of single ions would be greater for a poor micelle former than for a good one. Similarly, since it is the single ions or molecules which are adsorbed, surface active agents which are poor micelle formers can be expected to be good, that is, fast, wetting agents.

Among the anionic surface active agents the most common ones are salts of fatty acids, alkyl sulfates, and alkyl aryl sulfonates. Comparison of the wetting ability of the three groups shows that the sulfonates are the best wetting agents, that is, cause fastest wetting; the soaps from fatty acids, the poorest; and the sulfates, intermediate (53).

In the ordinary commercial preparation of the alkyl aryl sulfonates a mixture of isomers is formed, all of which exhibit more or less branching of the carbon chain (52). In contrast salts of fatty acids and alkyl sulfates usually have straight carbon chains. This may explain the differences in wetting ability among the three groups.

Change in Free Energy in Wetting

As is indicated in the Introduction, the change in free energy for wetting is dependent on the surface and interfacial tensions. In the case of the wetting of fabric the solution-fabric interface is of interest, but, unfortunately, the boundary tension at this interface is not directly measurable. Considerable evidence has been amassed, however, to indicate that equilibrium behavior at the solid-liquid interface closely parallels equilibrium behavior at the liquid-air interface.

Bartell and Greager (7), in studying the wetting of pigments, found a relationship between adhesion tension $\gamma_S - \gamma_{SL}$ and liquid absorption. The latter is the amount of liquid required to wet a given amount of powder using the Gardner-Coleman technique. Adhesion tension can be obtained from the contact angle of the liquid on the solid and the surface tension of the liquid.

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} = A_{SL}$$

Bartell and Hershberger (8a) wished to compare liquid absorption values with interfacial tensions for the pigment-organic liquid pairs under consideration. These interfacial tensions themselves were not measurable, but the authors reasoned that because the pigments and water are both polar the interfacial tensions obtained from measurements of the series of organic liquids in contact with water ought to fall in the same order as the interfacial tensions of the liquids contacting the pigments. They found that a plot of liquid absorption vs. water-organic liquid interfacial tension gave a series of straight lines (one for each pigment), provided there was zero contact angle. They concluded that the interfacial tensions at the pigment-organic liquid interfaces were in the same order as those at the corresponding water-organic liquid interfaces.

Osterhof and Bartell (37) tabulated the energy quantities associated with wetting a series of solids and the surface or interfacial tension involved. They suggested that relative values of solid-liquid interfacial tensions for a series of liquids against one particular solid might serve to measure wetting. Because these tensions are not directly measurable, they suggested that, as a substitute, adhesional tension be used as a measure of wetting.

A comparison of Hansen and Craig's data (29) on adsorption of aliphatic alcohols and acids on carbon black with the surface tensions as reported by Ward and Tordai (58) supports the hypothesis that solute molecules which lower the surface tension also lower the interfacial tension at a polar-non-polar interface.

Since experimental evidence suggests a close parallel in equilibrium behavior at solid-liquid and liquid-air interfaces, it appears reasonable to suspect that such a parallel also exists between the kinetic behaviors at these interfaces. This idea furnishes the broad basis for seeking a correlation between rates of wetting and of surface tension depression. Such a correlation would be extremely useful, for detailed studies of rates of surface tension depression capable of supporting quantitative mechanistic theories appear to be within practical range of existing experimental techniques, while this is not true of solid-liquid interfacial tensions.

Decrease in Surface Tension with Time

For many years it has been known that the surface tensions measured on newly formed surfaces of some solutions were higher than the equilibrium values. The instant the new surface is formed, the surface has the same concentration as the bulk of the solution. For dilute aqueous solutions there are so few solute molecules present initially in the surface that one would expect the surface tension to be nearly that of water and even for more concentrated solutions the number of solute molecules in the surface initially would be small. However, as solute molecules are adsorbed in the surface, the surface tension decreases, finally reaching the equilibrium value. Many authors have reported such a change in surface tension with time.

In 1907 Milner (36a) measured the change in surface tension of sodium oleate solutions by the capillary rise method. He found that although the adsorption was completed in a period of a few minutes for more concentrated solutions, several hours passed before the surface tension of dilute solutions reached equilibrium. He attributed the delay in reaching equilibrium to the time required for solute molecules to diffuse into the surface.

Ghosh and Nath (27) followed the changes in surface tension of solutions of dyes and other complex organic compounds with time. They found that variation of surface tension was not regular but that maxima and minima were observed.

Lottermoser (33) helped to explain the minima which Gosh and Nath observed. He reported a study of the surface tensions of solutions of salts of fatty acids. If carbon dioxide was admitted to the surface of the solution, the surface tension reached a minimum and then increased slowly. However, when carbon dioxide was excluded, the surface tension did not rise above the minimum. If the surfaces were stirred after equilibrium was reached, the solutions regained their low surface tensions in less than one minute. No explanation was given for the rapid recovery of the equilibrium value.

In the discussion which followed Lottermoser's paper Adam (1) cited work he had done with alkyl pyridinium and alkyl trimethyl ammonium bromides. These compounds would be unaffected by presence of carbon dioxide. In the absence of added salt the surface tension of dilute solutions, less than 0.025%, fell slowly, reaching an equilibrium value between 30 and 36 dynes after several days. In contrast solutions as concentrated as 0.1% reached a minimum value in a very few minutes.

Adam attributed the change in surface tension to aging of the surface, not aging of the solution, because the surface tension determined on freshly blown bubbles in the bulk of the solution was the same regardless of the age of the solution and regardless of the surface tensions indicated by bubbles which had been blown previously and now exhibited lower surface tensions than initially.

Adam and Shute (2) gave a more complete account of their experiments and results a few years later, but they still offered no explanation for the slow fall in surface tension.

Bond and Puls (13) offered the first quantitative theory of the surface tension depression kinetics. They assumed a diffusion controlled process and presented the following relationships between surface tension and time:

$$\frac{\gamma - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-\frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}}$$

The surface tension at any given time is γ ; γ_0 and γ_∞ are the surface tensions initially and at equilibrium. $\tau = (\frac{\bar{q}}{c})^2 \cdot \frac{1}{D}$ in which D is the diffusion constant and $\frac{\bar{q}}{c}$ is the ratio of surface to bulk concentration at equilibrium.

In arriving at the surface tension-time relationship given above, Bond and Puls used the Gibbs adsorption theorem, $\bar{q} = \frac{\bar{c}}{RT} \cdot \frac{d\bar{\gamma}}{d\bar{c}}$. This relationship applies only to dilute solutions. In particular it does not apply in the region where the surface tension is constant, or nearly so, as the concentration changes. Their treatment of the diffusion problem was also intuitive rather than rigorous.

Bond and Puls used an oscillating jet to measure surface tension. However, they could see only four or five waves along the stream. They made no attempt to correct their figures for difference in flow rates between the bulk and the surface of the jet. As a result, their figure can not be relied upon.

McBain, Vinograd, and Wilson (35) used an elaborate film balance to study the decrease in surface tension of lauryl sulfonic acid over periods up to an hour. They offered no theory to explain the change in surface tension.

Tartar, Sivertz, and Reitmeier (55) followed the surface tension of sodium alkyl sulfonates over long periods of time, 100-150 hours. Although they were seeking an understanding of the process by which surface tension changed with aging of the surface, they commented that their experiments did not clarify the process. They did note, however, that below the critical micelle concentration equilibrium was reached more rapidly with increase in concentration.

Ruyssen (46) reported that the surface tension of saponin solutions reached a minimum within four to five hours and the value remained constant for ten to 24 hours. Later irregularities he attributed to vaporization and hydrolysis.

In studying saponin solutions Boutaric and Berthier (14) measured the surface tension from the surface age of two minutes to two hours. The rate law which appeared to fit their data

$$\frac{\gamma - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-at}$$

was only slightly different from that of Bond and Puls, the main difference being the exponent on t.

Dognon and Gougerot (21) studied the surface tensions of sodium sulfolaurate, sodium oleate, and sodium glycocholate. These compounds offer considerable variation in rigidity of film and speed of orientation of solute molecules in the surface. From their data they suggested the law

$$\frac{\gamma - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-a\sqrt{t}}.$$

This is equivalent to the equation proposed by Bond and Puls (13) except that the constant a is less specific than the constant in the earlier law. Dognon and Gougerot claimed that their law, with the square root of t, gave a better fit for all of the compounds tested by them and that it gave a better fit to the data obtained by Boutaric and Berthier than when the first power of t was used. They pointed out that the agreement was least good when the solute molecules gave rigid films or, at least, oriented themselves slowly in the film. The authors claimed that there was no physical basis for picking the square root of time. However, if the lowering of the surface tension is diffusion controlled, one would expect the square root of t term, just as Bond and Puls suggested. Instead of accepting the law involving the square root of time Dognon and Gougerot pointed out that Boutaric and Berthier's expression is that of a monomolecular reaction and presented arguments used to arrive at this expression. Because it is adsorption at the surface which causes the change in surface tension, the surface covered is related to the decrease in surface tension. The rate of adsorption is proportional to the rate of covering the surface with surface active molecules and to the rate of increase of the fraction of the surface covered. This is also proportional to the fraction of the surface not covered.

$$\frac{ds}{dt} = \frac{d\theta}{dt} = a(1 - \theta)$$

where s is the surface covered and θ is the fraction of the surface covered. Integration gives

$$\frac{1 - \theta}{1 - \theta_0} = e^{-at}$$

θ_0 is the initial value of θ and is not zero. These authors also asserted that the initial surface tension might be different from that of pure water because surface active molecules would be dispersed in the fresh surface just as they were in the rest of the solution.

The fraction of the surface covered is expressed in terms of surface tension as follows:

$$\theta = \frac{\gamma_w - \gamma}{\gamma_w - \gamma_\infty} \qquad \text{and} \qquad 1 - \theta = \frac{\gamma - \gamma_\infty}{\gamma_w - \gamma_\infty}$$

When these values are substituted into the rate equation, it becomes

$$\frac{\gamma - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-at}$$

where γ_0 may not be equal to γ_w.

This law implies two hypotheses.

1. The surface pressure is proportional to the surface covered by the solute molecules, or in other words, the surface film is fluid. The proportionality would not be expected to be true if the orientation of the molecules is slow or if the film is rigid.

2. The rate of adsorption is proportional to the remaining free surface. There is no evidence to indicate whether or not this is true.

Since the data of Dognon and Gougerot did not fit this law, they proposed that the rate is proportional to the remaining free surface raised to the nth power.

$$\frac{d\theta}{dt} = a(1 - \theta)^n$$

After integration and substitution, the equation becomes

$$(\gamma - \gamma_\infty)^{1-n} - (\gamma_0 - \gamma_\infty)^{1-n} = at$$

The authors found that, for films in which the molecules oriented themselves practically instantaneously, at short times the data fit the equation well for n = 2, but the agreement was less good for longer times. For materials giving rigid films in which the molecules orient slowly the value of n appeared to be near 3 but the fit was not good for either long or short times.

In answering Dognon and Gougerot, Boutaric and Berthier (15) quoted the integrated equation as $\gamma - \gamma_\infty = (\gamma_0 - \gamma_\infty)e^{-a\sqrt{t}}$. To obtain this equation Boutaric and Berthier assumed that n in the differential equation above was one. They also used the square root rather than the first power of the time, but they said there is no reason to choose the exponent for t to be $\frac{1}{2}$; in its place they proposed to determine what values the exponent takes under different circumstances. They found that for the bile salts they used in their tests the exponent varied from 1.13 for 0.10 g./liter to 0.33 for 1 g./liter. They offered no explanation for this variation.

In 1943 Addison began a series of articles on the properties of freshly formed surfaces (3-6). Although he obtained data on the decrease in surface tension with time, he did not discuss it in relation to rate laws.

At the same time that the first of Addison's results appeared, Ward and Tordai (56) reported that diffusion could not be the controlling factor in the decrease in the surface tension with time. Their reason was that the decrease would be much faster, by a factor of 10^7 to 10^9, if it were diffusion controlled. They proposed that diffusion to the surface must be followed by a process of high activation energy. From their work in decreasing the surface area of a film, they concluded that there is an activation energy for desorption as well as for adsorption.

In two articles in 1945 Ross (44, 45) compared the theory of Bond and Puls based on thermodynamics to that of Doss (22) which is based on kinetics. Doss considered only the diffusion to the surface and ignored any movement out of the surface. For that reason the treatments of Bond and Puls on one hand

and Doss on the other can agree only when diffusion from the surface is negligible.

In some cases Ross found that the data fit the equation

$$\gamma - \gamma_{\infty} = (\gamma_0 - \gamma_{\infty})e^{-\frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}}$$

and in other cases a better fit was obtained from

$$\gamma - \gamma_{\infty} = (\gamma_0 - \gamma_{\infty})e^{-at}.$$

A somewhat different mechanism is proposed by Ward and Tordai (57). They defined the region directly below the surface and a few molecular diameters thick as the subsurface. In the initial stages of the formation of the adsorbed layer, solute molecules diffuse from the bulk to the subsurface more slowly than they pass from the subsurface to the surface. This assumes that equilibrium is established instantaneously between the surface and the subsurface. Ward and Tordai claimed the instantaneous achievement of equilibrium because initially the surface is nearly empty and every molecule arriving at the surface is likely to find an empty site and be adsorbed. The concentration of the subsurface drops to zero almost immediately.

As adsorption continues, the chance that a molecule of solute will arrive at a portion of the surface already occupied increases. These molecules will remain in the subsurface and as the concentration increases, some of them will diffuse back into the solution. Eventually the concentration of subsurface and bulk of solution become equal.

Ward and Tordai suggested two sets of equilibrium conditions which would simplify obtaining a rate expression: if subsurface concentration could be known, then diffusion into and out of the subsurface could be calculated; or if the surface and subsurface were in equilibrium, the subsurface concentration could be known from surface tension measurement. These authors said that neither Ross nor Doss included back diffusion from the subsurface in their theoretical treatments and they mistakenly assumed the concentration immediately below the surface was equal to the bulk concentration at all times. Ross made a further error in assuming polymolecular films.

Although Ward and Tordai agreed with the theory which Bond and Puls set forth, they claimed that the integrated form of the equation is incorrect. In deriving their own value for the surface concentration Ward and Tordai arrived at a complex and involved equation which must be evaluated by graphical integration. Values for the diffusion constant obtained from the rate equation should agree with corresponding values from other sources only if the activation energy for entering the surface is zero or small. However in applying their treatment to Addison's data for alcohols in water, they obtained values for diffusion constants which their theory could not explain. They suggested that the lack of fit could be attributed to the fact that the value Addison quoted as the equilibrium surface tension was not the true equilibrium value.

Burcik (16-19a) has reported several studies in which he has used the vibrating jet technique to measure the rate of lowering of surface tension of detergent solutions. He has discussed rate of lowering in relation to foaming and detergency and has discussed the effect of pH and added electrolytes on the rate of lowering. However, he has never attempted to formulate a rate law which would account for the decrease in surface tension; his data were also obtained without proper consideration of applicability of the vibrating jet equations or methods of surface age estimation.

Bartholome' and Schäfer (10) studied both the wetting of fabric by canvas disc wetting tests and the time dependence of surface tension. They found that speed of wetting of fabric was not related to equilibrium surface tension. For the reagents used equilibrium surface tensions were reached only after a matter of hours or days. The authors found that their data were represented by the equation

$$\gamma_{H_2O} - \gamma = \frac{a}{\frac{b}{\sqrt{t}} + 1}$$

where a and b are constants. Evidently $a = \gamma_0 - \gamma_\infty$; in addition Bartholomé and Schäfer asserted that

$$b = (\gamma_0 - \gamma_\infty) \pi^{\frac{1}{2}} (2\bar{c}_0 LkTD^{\frac{1}{2}})^{-1}$$

(D is the diffusion constant; L, the constant for two dimensional phase equilibrium; T, absolute temperature; k, Boltzman's constant.) No effort was made in their paper to justify this assertion, but by comparing their equation with that of Bond and Puls, it was found that the equations were essentially identical to terms first order in $t^{\frac{1}{2}}$, and it is therefore presumed that they obtained it by an intuitive argument of similar character.

These authors consider the reaction to be diffusion controlled and to have no energy barrier. Immediately after a new surface is formed the concentration of solute near the surface falls a maximum amount. As time passes, material diffuses into the region near the surface bringing the concentration in that region up to the concentration of the interior of the solution and providing more solute molecules to be adsorbed into the surface. The dependence of surface tension on time can be found from the relationship between surface concentration and surface tension on one hand and the rate of diffusion on the other. The former quantity the authors claimed could be obtained from measurement of the spreading pressure with a Langmuir balance. This method would not be available for more readily soluble materials.

Lange (32) continued with the equation Bartholome′ proposed, pointing out that, when $t = b^2$, $\gamma_{H_2O} - \gamma = a/2$. Thus b^2 represents the time required for the surface tension to fall half way to equilibrium. Lange called the angle of the initial slope in a plot of γ vs $\sqrt{t}$ equal to β, and he used tan β

$$\left[= -\left(\frac{d\gamma}{d\sqrt{t}}\right)_{t=0} = \frac{a}{b}\right]$$

as a measure of the rate of fall of surface tension. He found that the ranking of a/b and the wetting time followed the same order. He pointed out that since many wetting agents have similar equilibrium surface tensions, values for a for those wetting agents would not differ appreciably and that most of the variation in the ratio of a/b comes from differences in b. However, he observed that the wetting time was related to b^2. Since b itself is proportional to the concentration, a plot of log of the wetting time vs. log of the concentration should be linear with slope equal to -2; Lange found that for the eleven wetting agents he used the data fit this line well.

Ward and Tordai (59) studied adsorption at liquid-air interfaces to determine the rate controlling factor. In elaborating on their statements of several years earlier they claimed that diffusion would supply solute molecules to the surface faster than they are adsorbed and therefore diffusion could not be the rate-controlling process. There is evidence that dimers are present in solutions of some surface active agents and it has been suggested that decomposition of these dimers at the surface would determine the rate of adsorption. However, Ward and Tordai asserted that there are sufficient monomers present to fill the surface without any of the dimers decomposing. On the other hand they claimed that only molecules which collide with the surface with sufficient energy to clear a hole for themselves in the surface are adsorbed. Their data are in agreement with their proposed expression, based on the Boltzman distribution of energy.

Rideal and Sutherland (42) began a discussion of the factors which affect rate of surface tension depression by suggesting that the process is either governed chiefly by diffusion or else by an energy barrier to surface entry. Calculations based on their data and on Addison's would indicate that surface tension lowering is dependent on the orifice used. They suggest that there is movement of solute to the surface because of flow of the liquid as well as by diffusion and that movement of liquid within the jet depends upon the following:

1. The entrance to the orifice.
2. The length and form of the pipe which forms the orifice.
3. The exit of the orifice.
4. The pressure of fluid surrounding the jet.
5. The oscillations of the jet.
6. The spreading pressure of the adsorbed surface active agent.

The authors considered these six points and their effect on the movement of solute from point to point in the jet.

Data of Rideal and Sutherland and of Addison for n-heptanol solutions indicate that surface tension decreases faster than can be accounted for by diffusion alone. However, diffusion of 3-methyl-1-butanol supplies solute faster than it is adsorbed. Rideal and Sutherland use this as evidence for an energy barrier to entrance of solute molecules into the surface and they claim that a similar barrier would also exist for the heptanol molecules. To over-ride the effect of this barrier, they suggest the effects of liquid motion discussed earlier in their paper.

Methods of Measuring Rates of Surface Tension Depression

Practically all the common methods of measuring equilibrium surface tension have also been used to obtain non-equilibrium values. In order to measure rate of change of surface tension, information concerning the age of the surface as well as the surface tension itself must be known for each measurement. Most of the methods used heretofore do not allow both pieces of information to be known accurately.

Milner (36a) used capillary rise to determine surface tension. In order to obtain a new surface he forced the liquid to overflow at the top of the capillary. Since the times involved were relatively long, several minutes to several hours, a small error in zero time would not seriously affect the results. However, in narrow tubes the amount of surface active agent in the liquid film which slowly drained back into the tube would affect the non-equilibrium surface tension values obtained and the apparent rate of decrease of surface tension. Error would also result because the height of the liquid in the capillary tube varied with time.

Tartar and his co-workers (55) used a similar method, subject to the same errors. Since the period of time which their observations covered was 100-150 hours, even a large absolute error in zero time would have little effect on the results. However, error from the liquid draining from the sides of the capillary back into the surface would be present.

Four investigators used the pull on a ring or a plate to measure the surface tension. Ghosh and Nath (27) and Lottermoser (33) made use of a DuNuoy tensiometer or a similar instrument. Ruyssen (46) and Dognon and Gougerot (21) obtained their data by means of the Wilhelmy plate method. With these methods it is not possible to determine zero time for formation of the surface with any degree of accuracy. This is partly because in most methods of producing a new surface the entire surface would not be formed at the same instant and partly because additional surface is formed during the measuring process. The first cause would not give a large relative error if long times were involved, but there would be no way of decreasing the error associated with the formation of new surface during the measurement.

Other methods such as drop weight (Ward and Tordai (56) and Quintin and Biro (39)), pendant drop (Ward and Tordai (56)), sessile bubble (Adam and Shute (2)) and (Tartar and others (55)), maximum bubble pressure (Adam and Shute (2)) and the film balance (McBain and others (35)) also involve a change in surface area as the surface tension changes. Thus, it is not possible to know the true zero time with any of these methods. Rate equations developed to fit data obtained by these methods would reflect the rate at which the surface area increased as well as the rate of fall of surface tension.

The measurement of surface tension of solutions by means of a vibrating jet of liquid has been used by a few authors (Bond and Puls (13), Addison (3), Burcik (16-19) and Rideal and Sutherland (42)). This method avoids the difficulties of the other methods but presents problems of its own.

In 1879 Lord Rayleigh (40) reported a series of experiments on jets issuing from non-circular orifices of various shapes. As a stream of liquid issues from an orifice, it has the same cross section as the opening. However, the surface tension exerts a force to make the surface area a minimum, that is, to make the cross section become circular. Momentum causes the motion to continue beyond the circular shape. If the orifice is elliptical in shape, the cross section of the jet varies in shape from an ellipse to a circle to an ellipse and so on, but the major axes of successive ellipses are rotated 90°. Rayleigh developed an equation relating the surface tension to the wavelength, the density of the liquid, the cross-section of the jet, and the pressure under which the jet flowed.

Pederson (38) continued the study of vibrating jets, giving consideration to the following suppositions on which Rayleigh's theory is based:

1. Deviations from the circular-cylinder form are exceedingly small. It is difficult or impossible to fit this in practice, as it is just the divergence from the circular form which makes it possible to determine the wave length.
2. The vibrations are executed without loss of energy. However, all liquids have some viscosity and the waves damp out.
3. The original velocity is the same over the whole cross-section of the jet. Pederson claimed that for the jets he used this was very nearly true.
4. The surface tension is constant. The surface tension of pure liquids is constant or very nearly so but the surface tension of solutions may change with time.

Jets from even the best orifices which Pederson used were not free from alien vibrations. To improve the situation he suggested that a tube, rather than a plate, having an orifice of the proper shape would produce more nearly single vibrations. However, when a tube is used, the surface velocity of the jet is less than that at the axis, thus departing from one of the assumptions on which the theory is based.

Closely following the work of Pederson, Bohr (12) presented a paper giving the results of his work with vibrating jets. He emphasized the importance of producing a jet which executes vibrations of a single type. Since it was difficult to get pure vibrations near the orifice, Bohr's objective was to produce a jet which would be stable even at great distances from the orifice. He used the consistency of the wave lengths along the jet as proof of the exactness of his method and the purity of the vibrations.

Pederson and Bohr added terms to Rayleigh's original equation to correct for the effect of viscosity of the liquid and the amplitude of vibration.

Addison (3) studied the relation between rate of flow and wave length in the vibrating jet. Theoretically these should be proportional to each other, but he found that wave length increased faster than flow rate. He says that Rayleigh and Bohr attributed this effect to (a) the damping effect caused by viscosity of the liquid, (b) the increasing wave amplitudes which come with increasing flow rate, and (c) the inertia of the surrounding medium. He also stated that when liquids of low viscosity are used, the velocity gradient set up at the orifice from the axis to the surface of the jet would be maintained throughout the jet. This would cause the restoring force of the surface tension to act at an angle slightly different from 90° to the surface. Although he showed mathematically how this would affect the period of vibration, he stated that there was no practical method of making the necessary measurements to correct for this effect.

Instead of using the equation as Rayleigh, Pederson, and Bohr had developed it, Addison collected all the terms except the wave length and the relation between the rate of flow and the wave length into one term which he claimed was a constant for any one apparatus. The value of the constant was determined from the known surface tension of water and checked using three organic liquids.

Rideal and Sutherland (42) also used the vibrating jet technique to study the surface tension of solutions. They concluded that the rate of decrease of surface tension as measured by the vibrating jet was dependent on the orifice used, the smaller the orifice the more rapidly equilibrium was approached. They also showed that the results differed for the same orifice when the rate of flow was changed.

Although the vibrating jet method of measuring surface tensions of solutions has great potential, the method of calculation must be improved to account for variation in velocity over the cross section of the jet. If this could be done, accurate surface tensions could be obtained for any point along the jet. If the vibrating jet method is to be useful for the determination of the rate of surface tension depression, it is necessary to evaluate the surface tension accurately at a point on the jet. It is equally necessary to evaluate the true age of the surface at that point, and for this it is necessary to know the surface velocity of the jet, as contrasted with the mean velocity. Rideal and Sutherland (42) appear to be the first workers to recognize the existence of a problem in this respect, and their treatment of the problem was only approximate.

Measurement of Rate of Wetting

The methods commonly used to determine the wetting ability of solutions have been to measure the time required for a skein of yarn (23a) or a canvas disc (50) to sink in the solution. Obviously this is a measure of the rate rather than the degree of wetting. For the skein wetting test a specified amount of yarn is attached by a thread to a weight. The sinking time is measured from the time the skein enters the solution until it sinks to the point that the tension is taken off from the thread connecting the yarn to the weight. In the canvas disc test a circle of the fabric is held below the surface of the water and the time required for the disc to begin to sink because of its own weight is measured.

Within the range of five seconds to three minutes fair reproducibility is obtained when skilled persons repeat their measurements (48). However, in order for workers to compare results all must use the same type of yarn or of woven fabric and all must use the same techniques. At best the test is empirical and gives no insight into the mechanism of wetting.

Several workers (41, 51) have used a hydrometer to follow the extent of wetting of yarns or fabrics. As the cloth becomes more thoroughly wet, the buoyancy decreases. When high concentrations of wetting agents are used, the wetting may be rapid but not complete because of occluded air. This test has little advantage over sinking time tests and neither test is of any value in studying the mechanism of wetting.

MATERIALS, APPARATUS, AND METHOD OF PROCEDURE

Materials

Two anionic and one cationic surface active agents were used in this study. Santomerse D, a sodium decylbenzenesulfonate manufactured by Monsanto Chemical Co., is typical of the alkyl aryl sodium sulfonates used in packaged detergents. Areskap 100, monobutylphenylphenol sodium sulfonate is another anionic product manufactured by Monsanto. The cationic agent used was trimethyldodecylammonium chloride obtained from Research Division, Armour and Co.

Attempts to purify the anionic materials by recrystallization were unsuccessful. On precipitation from solution they form a waxy mass. No literature reference could be found which reported purification of either Areskap or Santomerse D or related compounds. Several authors have reported studies involving these materials but they either used the compounds as received or they did not report whatever purification they carried out. These materials were therefore used without purification (except for drying). The Santomerse D used can be expected to be heterogeneous as to position of substitution (alkyl group ortho or para to sulfonate group) and as to nature of alkyl group (straight chain or branched) and to contain a small amount (not more than 0.5%) of sodium sulfate. The

Areskap 100 used can be expected to be heterogeneous as to position of substitution, and it probably also contained a small amount of sodium sulfate.

Purification of trimethyldodecylammonium chloride was accomplished by crystallization from ethanol. The crystals formed readily as the solution cooled.

All the materials were dried to constant weight at room temperature over anhydrous magnesium perchlorate before use.

The water used in the surface tension measurements or in making up solutions was distilled from alkaline permanganate solution. The acetone and butanol used were purified by distillation using a 30 plate Oldershaw column at 10:1 reflux ratio. The boiling point of the acetone used was 55.2°C. at 739 mm. of pressure and of the butanol, 117°C. at 740 mm.

The solution with the highest concentration of each of the surface active agents was made up by weighing out the required amount of solid and diluting to volume. As these materials, especially the anionic ones, are quite hydroscopic, the weighing was done by difference and the weighing bottle opened for as short a time as possible. Other solutions were made up by dilution of more concentrated ones.

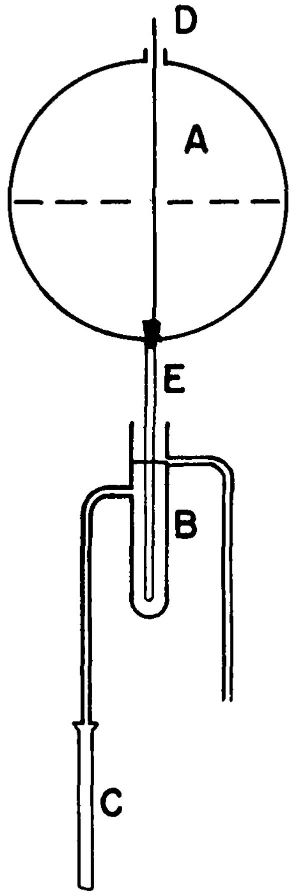
Apparatus for Measuring Dynamic Surface Tensions

The apparatus used in this study to measure dynamic surface tensions can be separated into the equipment used to produce the jet and that used to determine the wave lengths and the jet diameter.

In order to produce vibrating jets from which accurate surface tension data can be obtained, the apparatus must meet certain requirements. The orifice from which the jet issues must have a section of the form $r = a + b \cos 2\theta$, the rate of flow must be maintained constant, vibrations from the apparatus must not be passed on to the jet, and the apparatus must be easily cleaned.

The apparatus used is shown in Figure 1. It consisted of a main reservoir A, a constant head reservoir B, the tube containing the orifice C, and the connecting tubing. The main reservoir was a 5-liter, round bottom flask to which the female part of a ground glass joint was attached. Flow of liquid from this reservoir was controlled by a ground glass male plug attached to the glass rod D by which it was manipulated. The tube E was constricted so that the rate of volume flow from the main reservoir to the constant head reservoir slightly exceeded that from the constant head reservoir through the orifice, the excess being discarded through an overflow.

The constant head reservoir was made from a large test tube by attaching to it two side tubes on opposite sides and at different levels, the upper tube serving as an overflow. In order to prevent turbulence in the reservoir from affecting the stream, liquid was discharged into the reservoir near the



A MAIN RESERVOIR
B CONSTANT HEAD RESERVOIR
C ORIFICE TUBE
D ROD TO MANIPULATE PLUG IN DISCHARGE TUBE.
E DISCHARGE TUBE

Figure 1. Apparatus for producing the jet

(Scale: 1" = 6")

bottom of the tube, an appreciable distance from the side tube through which the liquid flowed to the orifice. The nickel orifice tube was attached to a short length of glass tubing which was connected to the discharge tube from the reservoir by means of a ball and socket joint. Two reservoirs were used, each with a different length of discharge tube, to give different pressure heads.

The entire apparatus with the exception of the orifice tube was made from glass and was cleaned with hot chromic acid cleaning solution before each test. The orifice tube was rinsed with acetone and double distilled water and dried before each use.

Vibrations in the entire apparatus were reduced to a minimum by mounting the parts on a rigid frame. The framework, shown in Figure 2, was made from DexAngle, manufactured by Acme Steel Co. Sufficient cross-bracing was used to hold it rigid. For some tests the orifice tube was clamped firmly to the supports. In other cases the connection was less rigid. Apparently more vibrations were transferred to the orifice tube when the connection was rigid; in such cases, the stream was less steady and fewer waves could be measured.

Rayleigh's equation from which surface tensions are calculated from vibrating jet behavior results from a development in Fourier-Bessel series of the velocity potential perturbation by the non-circular jet. Terms in this series are of the form

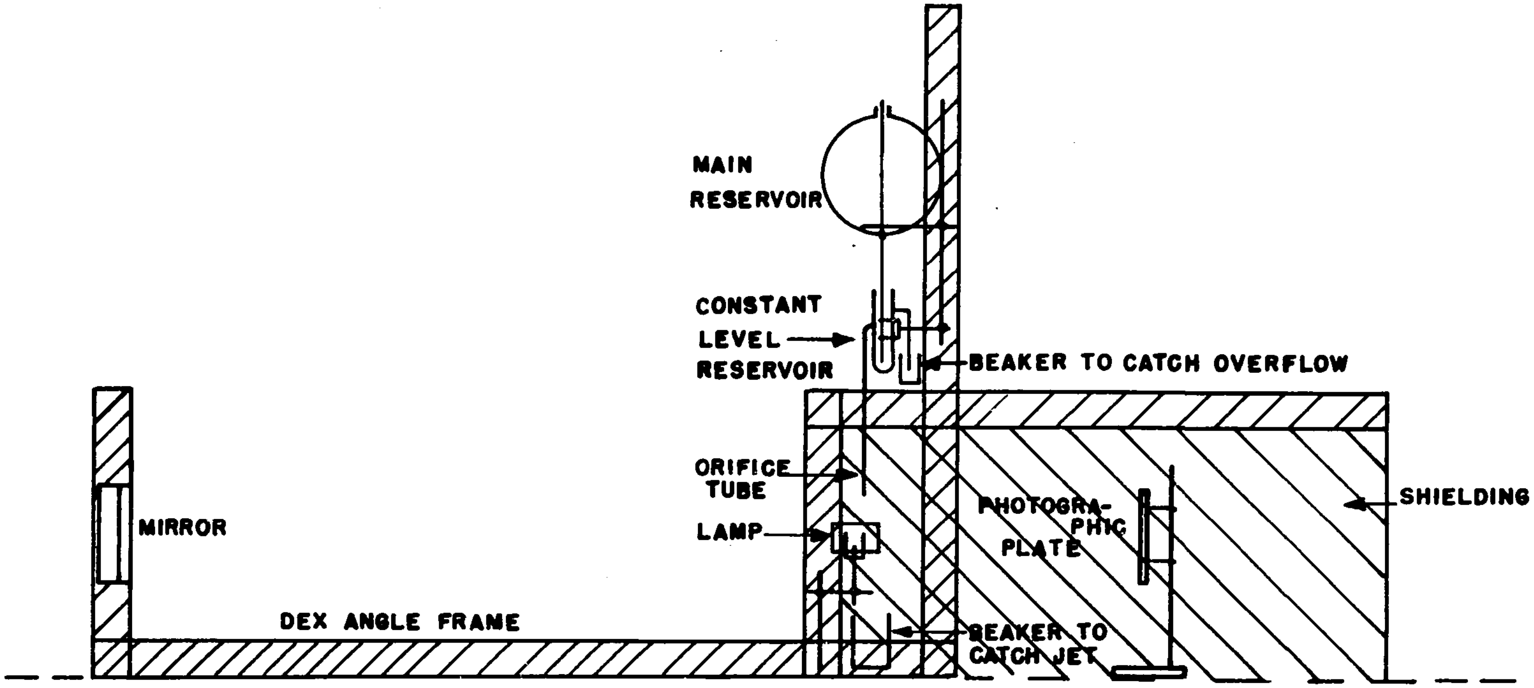


Figure 2. Arrangement of apparatus on DexAngle framework

(Scale: 1" = 20")

$\cos n\theta J_n(ikz)$, where n is an integer, z is the axial distance from the orifice, and J_n is Bessel's function of order n. Terms with high n are rapidly damped by viscous forces, but in order to make accurate surface tension determinations near the orifice it is highly desirable that the Fourier-Bessel series reduce to a single term. This can be accomplished by making the orifice section accurately of the form $r = a + b \cos m\theta$, in which case all terms in the series except the m^{th} have zero coefficients. If m = 2, the orifice section is nearly elliptical, the jet form is relatively simple to observe, and fabrication of an orifice to this section is reasonably practicable.

There should be no movement of molecules perpendicular to the axis of the jet except the movement associated with the vibration of the jet. This means that there can be no spreading of the stream as it leaves the orifice and no turbulence in the stream. To prevent the stream from spreading the edges of the orifice must be sharp. Turbulence results in particular from a sudden change in the diameter of the tube or stream. A fairly small orifice is chosen so that the liquid being tested will be conserved, but a delivery tube with a larger diameter is needed so that friction does not reduce the force with which the liquid flows from the orifice. If a plate orifice is used, turbulence must certainly be present and measurements made near the orifice would be of little value.

When a sudden change in diameter occurs, the effects of an unstable turbulence damp out as the stream travels. From his experience in hydrodynamics Professor Glenn Murphy, Head of the Department of Theoretical and Applied Mechanics, Iowa State College, advised that turbulence could be expected to disappear as the stream travelled a distance eight times the difference in the two diameters. However, for this work it was important that there be no turbulence in the stream even near the orifice. Professor Murphy further advised that turbulence could be avoided if the change in diameter occurred gradually over that same distance within the tube.

Besides having no sudden changes in diameter, it is important that the sides of the tube be absolutely smooth so that no eddies are created and disturb the flow. Unless a large amount of liquid is available for each experiment, it is important that the orifice be reasonably small, of the order of one millimeter in diameter.

In summary the requirements of the orifice are as follows:

1. The cross-section must be of the form $r = a + b \cos 2\theta$.
2. The difference between the major and minor axes must be small.
3. The edge of the orifice must be sharp.
4. There can be no sudden changes in the diameter of the tube in the neighborhood of the orifice.

5. The interior of the delivery tube near the orifice must be smooth.
6. The orifice itself should have an average diameter of the order of one millimeter.

Several attempts were made to construct a tube and orifice from glass capillary tubing and from six to eight millimeter tubing. In all cases it was difficult to shape the orifice correctly. When capillary tubing was used, the glass was held in a vertical position and heated evenly on opposite sides and squeezed gently with vise-grips. The tube was later cut or broken at the spot which had been heated. The amount of deformity from circularity depended on how hot the glass was and how much it was squeezed. Many orifices had to be constructed before one passed a visual inspection for elliptical shape. Attempts were made to soften larger tubing and let it shrink down onto a solid object which had the appropriate shape but to which the glass did not stick. No material was found which could be shaped accurately and to which glass did not adhere.

The idea of making an orifice from glass was abandoned in favor of constructing one by electroforming a tube on an accurately shaped mandrel. Drill rod, one-fourth inch in diameter, was chosen for the mandrel. It was shaped in a lathe to taper evenly from the original diameter to approximately one millimeter over 5 centimeters of length. The small tip extended about two centimeters beyond the taper. It was then polished by turning it at high speed in a lathe while carborundum backed by Apiezon was held against the metal. During this process special attention was given to the needle-like tip and to the junction of the main taper and the tip. After the polishing was completed, the diameters of the tip were measured at 10^{o} intervals to determine that the cross section of the mandrel had remained circular.

The tip was then modified to elliptical cross section by stroking the tip lengthwise between the first finger and thumb, carborundum having been placed on the thumb and finger. In order to approximate symmetrical erosion as closely as possible, right and left hands were used on alternate strokes, pressure between the thumb and finger was maintained as constant as possible, and the strokes were in the direction of the long axis of the mandrel.

The relative number of strokes at each position required to change a circle into an ellipse was calculated. The strokes were counted and when the predetermined number for one position was completed, the mandrel was rotated 20^{o} and the rubbing begun again.

When the difference between minimum and maximum axes was great enough to be satisfactory, the "diameters" or axes differing in orientation by 10 to 20^{o} were measured and plotted. A plot of $d = 2a + 2b\cos 2\theta$ was drawn where d is the "diameter", 2a the average diameter, and 2b is the difference between maximum and minimum diameters. Comparison of the points plotted from the measurements with the theoretical plot showed where the tip required further rubbing to give it the desired shape.

The mandrel which was actually used required 75,000 strokes to convert it to its final shape.

Electroforming requires a deposit which will adhere to the base well enough to accurately take the shape of the base and yet will release the base when it is desired to strip off the plating. Nickel will not adhere strongly when plated over chromium which has been oxidized slightly to make it passive. For this reason nickel was chosen as the material for the tube and the mandrel was plated with chromium. Because chromium bonds well to copper and copper to steel, a thin layer of copper was deposited on the mandrel followed by a thin chromium layer. The passivation of the chromium was accomplished by allowing the mandrel to remain in the chromic acid plating bath for a short time after the plating current was stopped.

Before the plating was begun, the mandrel was cleaned very thoroughly to remove all grease. It was washed in detergent solution, rinsed and air dried. Then it was dipped several times in trichloroethylene and again air dried. Further cleaning was accomplished by making the mandrel the anode in an alkaline solution and allowing electrolysis to take place for several minutes. The alkali was neutralized by dipping the mandrel in five percent hydrochloric acid. At that time the mandrel was ready for copper plating.

The solutions, temperatures, current or current densities, and the length of time for plating are given in Table 1. These data are adopted from the work of Blum and Hogaboom (11).

Because the area on which the nickel was deposited increased as the plating progressed, the current had to be increased to keep the current density constant. The nickel plating process was terminated when it was considered that the plating was thick enough to withstand the force required to strip it from the mandrel. Near the top of the plating, the large diameter of the mandrel, the plating was about 0.15 cm. thick. At the tip end it was much thicker, about 0.25 cm.

Two additional steps were required before the plating was removed from the mandrel. The end of the mandrel and plating was ground off on an emergy wheel to expose a predetermined cross section of the tip, one which earlier measurements had shown to be the desired shape. The end of the plating and mandrel was then polished on a metal polishing wheel until no scratches were observable under a hand lens. Next a square shoulder against which force could be applied was turned in a lathe on the other end of the plating. While it is being removed, the plating must not be allowed to turn on the mandrel.

For verification of the shape of the orifice the axes of the orifice itself were measured at various orientations.

Table 1. Solutions and conditions for electroplating

Process	Solution	Temperature	Current or current density	Time
Alkaline cleaning	23 g. Na_2CO_3 23 g. Na_3PO_4 10 g. NaOH Make up to one liter	75°C.	0.4 amps	5 minutes
Copper plating	26 g. CuCN 35 g. NaCN 30 g. Na_2CO_3 45 g. Rochelle salt ($NaKC_2H_4O_2 \cdot 4\ H_2O$) Make up to one liter	70°C.	Cathode-- 7 $amps/dm^2$ Anode 3 $amps/dm^2$	20 seconds
Chromium plating	400 g. CrO_3 Make up to one liter	45°C.	Cathode-- 3 $amps/dm^2$	10 minutes
Nickel plating	240 g. $NiSO_4 \cdot 6\ H_2O$ 45 g. $NiCl_2 \cdot 6\ H_2O$ 30 g. boric acid Make up to one liter	43°C.	Cathode-- 0.1-0.3 $amps/dm^2$	2½-3 days

These measurements were compared with a cosine curve having the same maximum and minimum. The agreement of the two curves for the orifice used was considered satisfactory. The theoretical curve and experimental points are shown in Figure 3.

Apparatus for determining the wavelength and the jet diameter

In the vibrating jets used the maximum and minimum diameters differed by no more than 0.009 cm. and the change from maximum to minimum occurred very gradually over several millimeters. Because of these facts it was impossible to determine the distance from one maximum to another on the stream itself. Several authors have reported ways to magnify this difference. The method used here is similar to that used by Rideal and Sutherland (42). Each wavelet acts as a lens focusing the light passing through the stream. When a screen is placed behind the stream at a distance of one focal length, parallel lines of light appear which are perpendicular to the stream. The distances between the lines represent the wavelengths of the vibrations in the jet. Figure 4a is a schematic presentation of the light being focused by the stream; Figure 4b is a typical photograph showing the focused lines of light.

To avoid magnification caused by divergent light, it was desirable to illuminate the jet with parallel light. This was obtained by reflecting light from a parabolic mirror. The

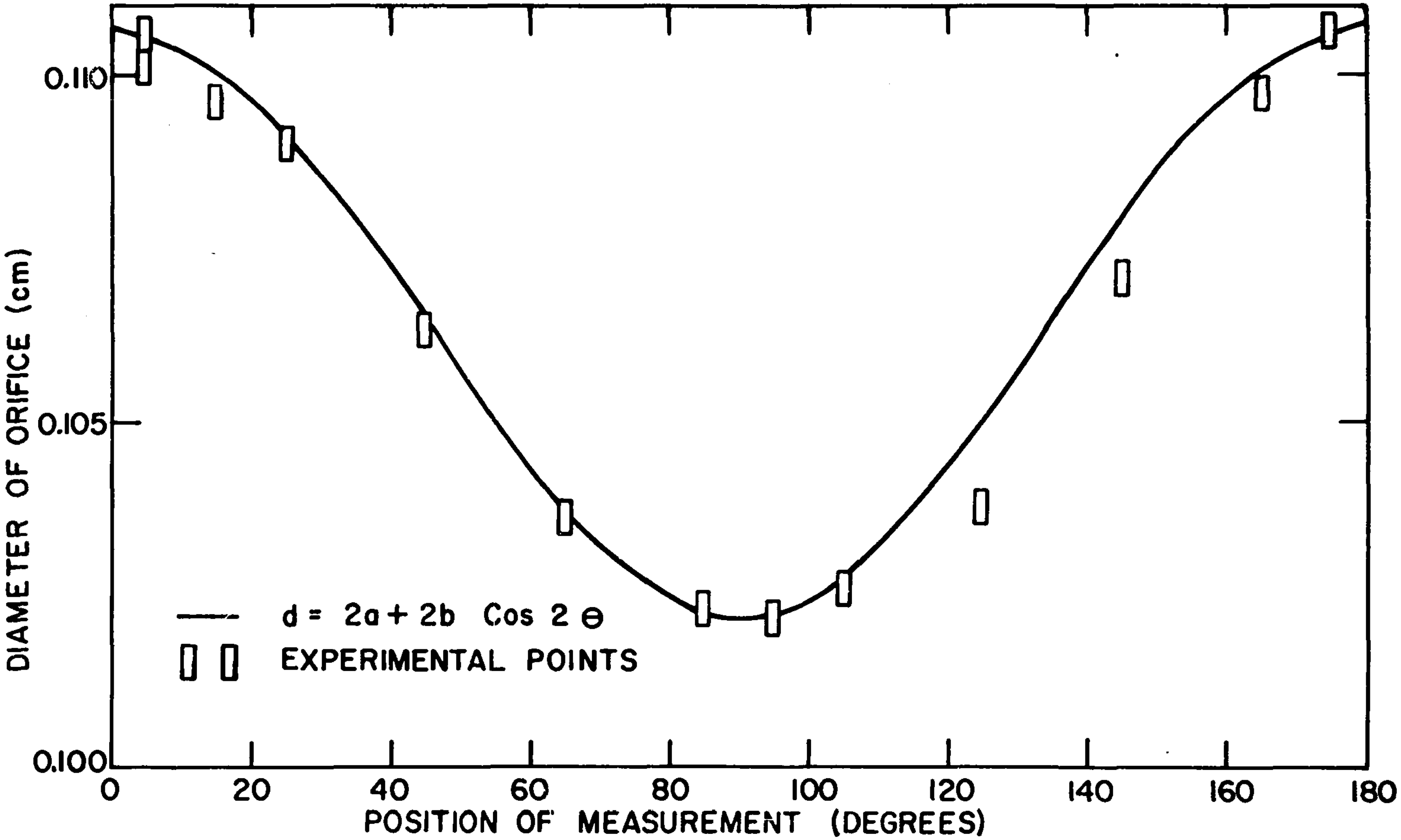
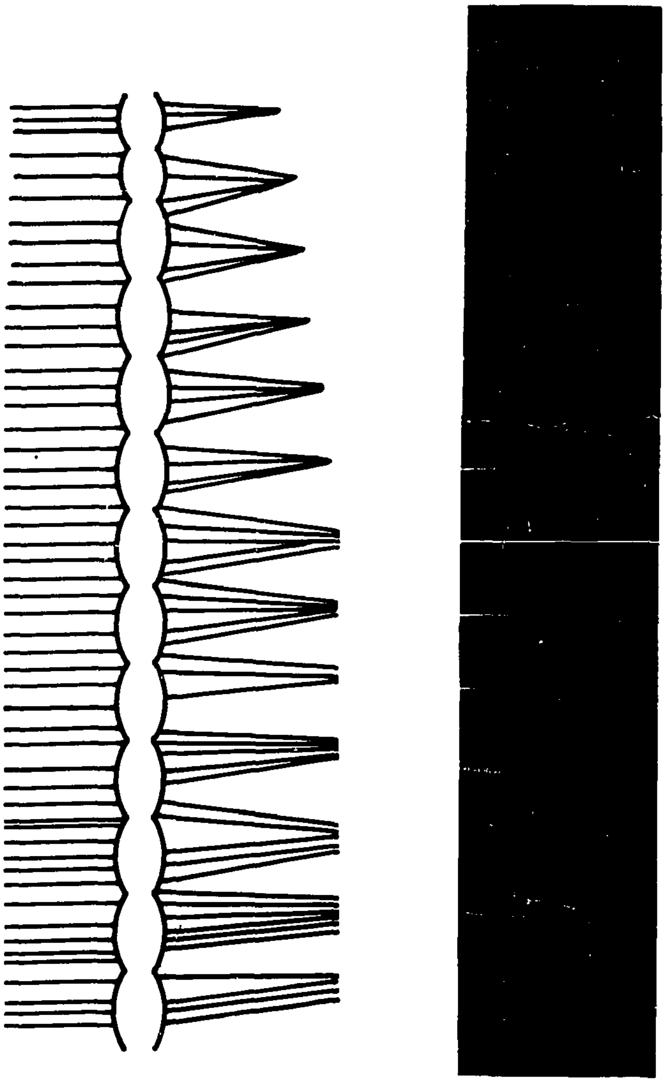


Figure 3. Shape of the orifice



a.

b.

Figure 4. Focusing effect of the jet

a. Schematic diagram of jet focusing light

b. Photograph showing focused and unfocused lines mirror had been purchased by Dr. Lawrence Bartell from the Mayfloor Products Corp., Katonah, N. Y., for use in a telescope. Its diameter was approximately ten inches and its focal length, 76 inches. The light source was a 40-watt "Zirconarc" photomicrographic lamp from the Fish-Schurmann Corporation. It was made to approximate a point source by enclosing it and using only the light issuing through a hole three-eighths inch in diameter. The focal point of the mirror was located by moving the light source nearer to and farther from the mirror until the shadow of the markings on a transparent scale fell exactly on the markings of a duplicate scale which was placed at some distance farther from the mirror.

Because it is both difficult and inconvenient to measure the wave lengths while the stream is flowing, photographs were made which could be examined at one's leisure. No camera as one usually thinks of it was needed as the wavelets in the stream serve to focus the light. Apparatus for taking photographs consisted of an arrangement for holding the photographic plate, shielding to prevent stray light from striking the plate, and some means of controlling the exposure time.

The photographic plates used were 4" x 10" IV N Spectrographic plates from Eastman Kodak. They were held firmly in a rectangular plate holder during the exposure. The holder was clamped to a ringstand and its position could be varied by moving it vertically on the rod or by shifting the position of the ringstand.

DexAngle framework was extended horizontally from the supports on which the jet apparatus was attached. The top and sides of this were covered with cardboard to form a housing which protected the plate from stray light. In the shielding between the mirror and the jet a slit was cut so that light could strike the jet. This opening was adjustable so that very little besides the jet was illuminated.

The exposure was made by admitting light through the slit for a predetermined time. Since the exposure times were relatively long, from ten seconds to five minutes, the exposure could be controlled manually and the timing done with a stopwatch.

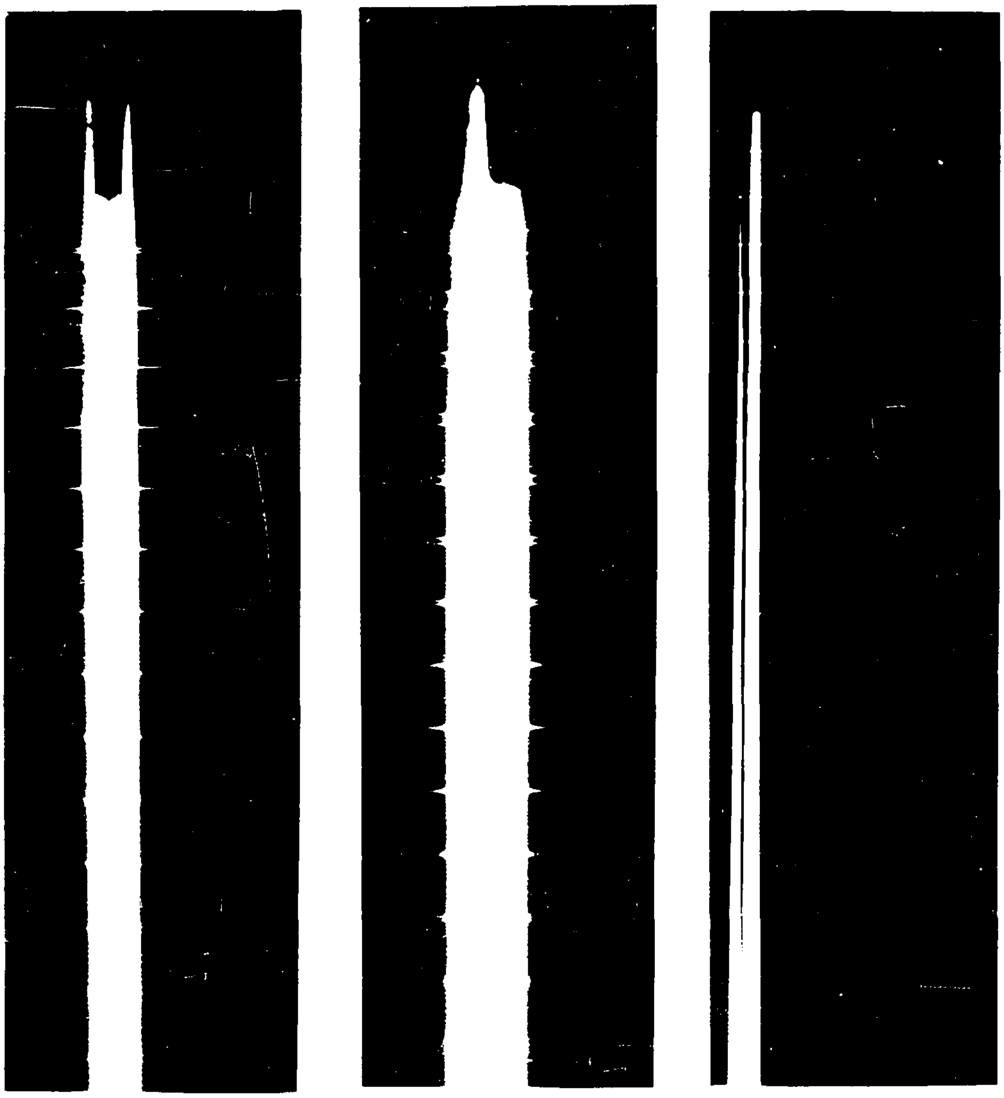
The focal length of the wavelets increased along the stream as the wave length increased. This increase came because of increase in stream velocity due to gravity. When solutions of surface active agents were used, a further increase in wave length resulted from the decrease in surface tension. If the change in focal length along the stream was significant, not all the parallel lines formed by the light passing through the jet could be brought into focus at any one distance from the jet. For this reason a series of pictures was taken at different distances so that every line appeared in reasonably sharp focus on at least one plate.

In order to determine the velocity of the stream it was necessary to know its diameter. Measurement of the shadow of the jet on the plates used for measuring wave length did not give a sufficiently accurate value for the diameter. Photographs were therefore made with a real camera which gave a magnification of about six. The picture included the tip of the orifice tube so that distances along the stream from the orifice could be determined. A glass rod whose diameter was accurately known was included in the photograph and used to determine the exact magnification.

All measurements to determine wave length or jet diameter were made by means of the Cambridge Universal Measuring Machine. This is essentially a travelling microscope and an accurate scale. With this machine it is possible to measure with a precision of $\pm$ 2 x 10^{-4} cm.

Photographs

Several of the pictures have been reproduced here. Figures 5a and b are pictures taken of a vertical jet of water with a velocity of 233.0 cm./sec. The white vertical strip resulted from light which passed through the slit and exposed the plate. The shadow extending into the slit at the top is part of the orifice tube. The shadow of the jet itself shows faintly at the tip of the tube. The horizontal lines are



a. b. c.

Figure 5. Water jets showing variation in focusing ability and dependence of wavelength on velocity

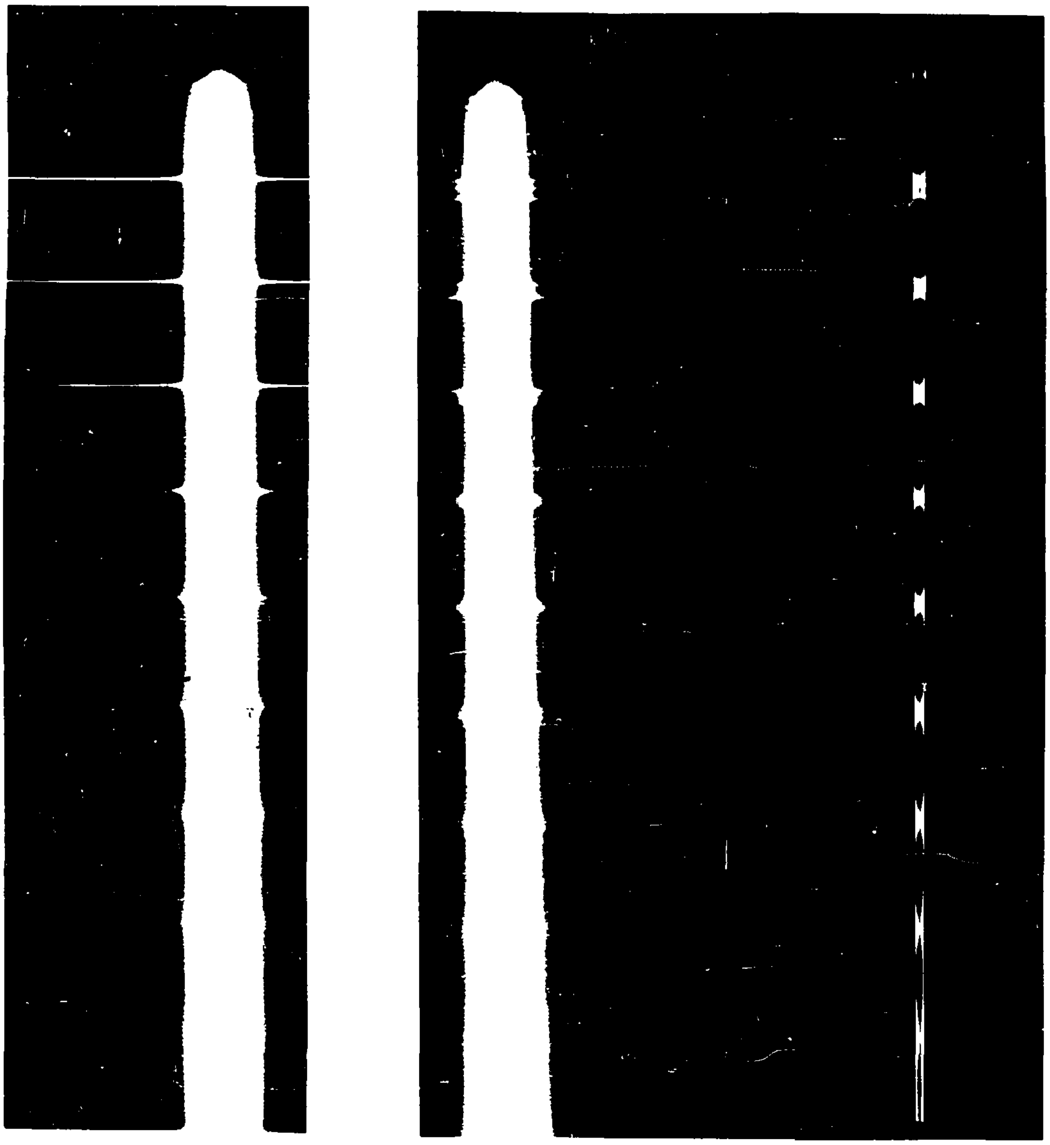
a. v_o = 233.0 cm./sec., 12 inches between plate and jet

b. v_o = 233.0 cm./sec., 21 inches between plate and jet

c. v_o = 187.1 cm./sec., 6 inches between plate and jet formed as the light striking the wavelets in the jet is focused as is shown in Figure 4. As the jet flowed, the velocity increased because of gravity, and the increase in velocity along the jet caused the waves to increase in length and the lines in the photograph to be farther apart. Further, the focal length of each wave acting as a lens increased as the wave length increased and as the waves damped out. The picture in Figure 5a was obtained with a photographic plate 12 inches from the jet. In it the third, fourth and fifth lines are narrow and have sharp edges. In Figure 5b, taken with 21 inches between the jet and the photographic plate, the ninth, tenth and eleventh lines are in best focus. The lines which focus in front of the plate are broad but fairly sharp while those which focus behind it are progressively more fuzzy and dim.

Figure 5c shows the lines from a vertical jet of water at a velocity of 187.1 cm./sec. Comparison of lines in Figures 5a and 5c shows that at lower velocities the waves have greater focusing ability and the lines are finer than when the wave lengths are longer. Very accurate measurements of the wave length could be made easily on photographs similar to Figure 5.

Figure 6a shows a picture of an acetone jet having a mean velocity of 252.6 cm./sec. The wave lengths are longer than for water jets at the higher velocity and the lines are broader. Even the sharpest lines in the pictures for acetone are not as fine as the focused lines for water. Because of



a.

b.

Figure 6. Acetone jet

a. 18 inches between plate and jet

b. 30 inches between plate and jet, glass rod used to "collect" light the lower viscosity of acetone the change in wave amplitude along the stream is smaller for acetone than for water.

The right hand part of Figure 6b shows the results of an attempt to concentrate the light in the lines. A three-fourths inch glass rod was placed between the jet and the photographic plate in such a way that the light passing through the rod was focused on the plate. Although the rod collected the light as predicted, the spots on the plate were not sharply enough defined to permit accurate measurements. A similar arrangement using a better lens should give improved results and allow pictures to be made with shorter exposure times.

Pictures of butanol jets are shown in Figure 7. The well-focused lines in Figures 7a and 7b are very fine compared to similar lines for either water or acetone. Only one line is in good focus in each of the pictures, indicating that the focal length of the wavelets changed rapidly along the stream. The relatively high viscosity of butanol causes the waves to damp out quickly. Even at a distance of 64 inches between the stream and the photographic plate, Figure 7c, it is only the fifth line which is in best focus. The fifth wave in the acetone stream shown in Figure 6b had a focal length in the neighborhood of 30 inches. The focal length of the corresponding wave for water in Figure 5a was slightly more than 12 inches.

Figure 8 shows pictures of jets of Santomerse D solution. They are typical of the pictures obtained from jets

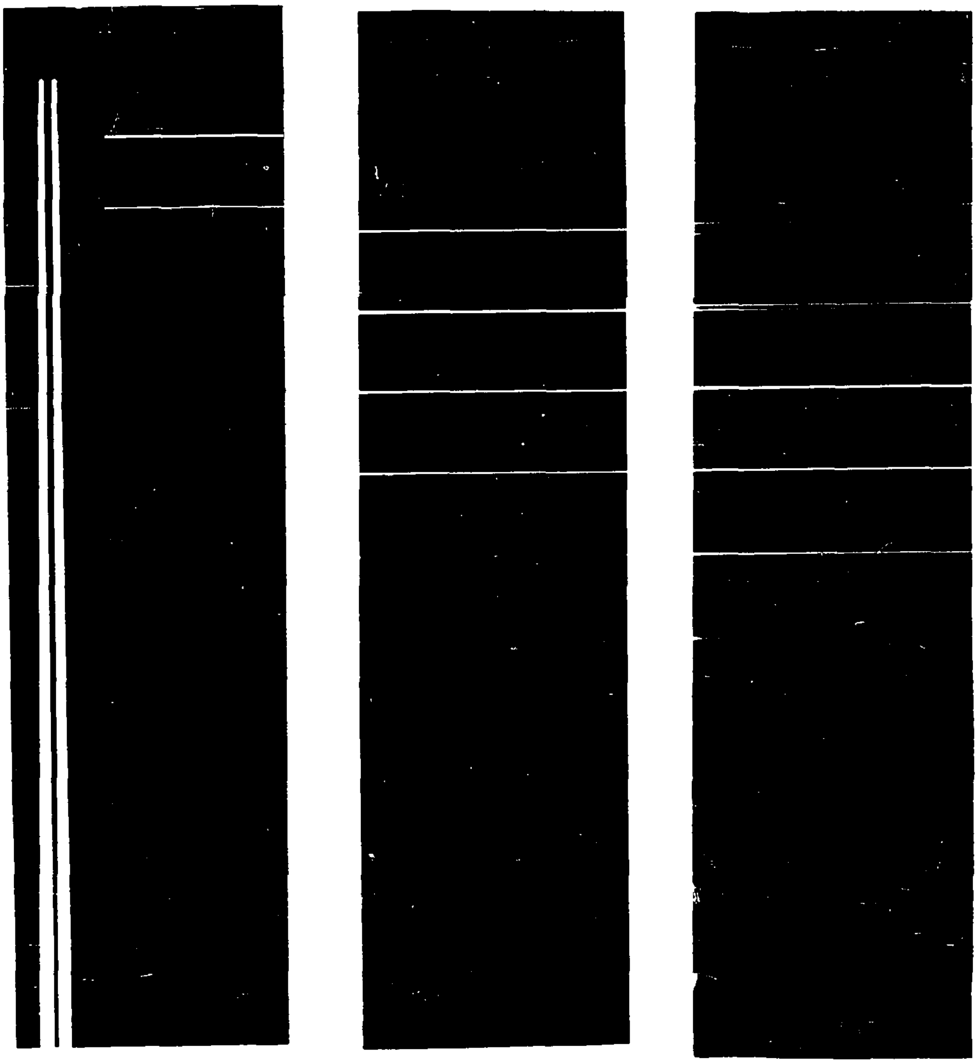
a. b. c.

Figure 7. Butanol jets

a. 15 inches between plate and jet

b. 24 inches between plate and jet

c. 64 inches between plate and jet



a. b. c.

Figure 8. Santomerse D solution jets

a. 12 inches between plate and jet

b. 33 inches between plate and jet

c. 45 inches between plate and jet

of solutions of surface active agents.

With the long exposure needed when the distance from the plate to the jet was large, the image of the slit was so much over-exposed that the position of the end of the orifice tube could not be determined exactly. This is apparent in Figure 6 and others. In Figure 8a light striking part of the picture was blocked out after a few seconds of exposure. As a result the end of the orifice tube is easily located and the shadow of the jet is clearly seen.

Procedure for Collecting Data

Dynamic surface tension measurements

Before each test, all the glass parts used in producing the jet were cleaned with hot chromic acid cleaning solution and rinsed with double distilled water. The orifice tube was rinsed with acetone and double distilled water. The constant head reservoir and the orifice tube were dried before each use. Because of the size of the main reservoir, it was not oven-dried but it was rinsed with the liquid to be tested before it was filled.

At the beginning of the test all the parts were assembled and the reservoir filled with liquid. The jet was allowed to flow long enough so that the stream could be adjusted to flow vertically. This was done by lining the stream up with a plumb line. Before any photographs were made, the parallel lines of light were focused on a screen in the plate holder and the plate holder moved to various distances from the jet to determine in what positions photographs should be made.

The room was darkened and the light from the Zircon lamp covered while the screen used for focusing was replaced by a photographic plate. The cover was taken from the light and the plate exposed. For pictures made with the plate near the stream as little as ten seconds was a sufficient exposure, but because of the spreading of the light, the pictures taken at the greatest distance from the jet required up to five minutes exposure. The exposure was stopped by covering the light source again.

The plates were developed five minutes in Eastman Kodak D-19 developer, rinsed under running water and placed in Eastman Kodak F5A fixer for 10 minutes. After that they were washed in running water for 10 to 30 minutes and dried.

The relative positions of the lines and the orifice were obtained by means of the measuring machine. Triplicate measurements were made on each line and the three values averaged. For the sharpest, bright lines the agreement between two measurements was ± 0.0005 cm. However, measurement of the more diffuse, dim lines was not nearly so accurate. Reproducibility in measuring the least sharp lines was ± 0.005 cm. The position of the orifice was even more difficult to locate accurately. Its shadow appeared on the plate but overexposure of the surrounding area caused the shadow to have extremely fuzzy edges. The position of the orifice was known with an accuracy of no more than ± 0.05 cm.

Table 2 is typical of the raw data for a test.

The volume rate of flow was determined by measuring the length of time required to fill a volumetric flask. Agreement between measurements was ± 0.005 $cm.^3$ per second.

The temperature of the liquid in the main reservoir was $25^{\circ} \pm 1^{\circ}C.$ for the tests. Whenever the room temperature was such that the temperature of the liquid was outside this range, the main reservoir was warmed or cooled to bring the temperature of the liquid within this range.

Equilibrium surface tension measurements

All equilibrium surface tension measurements were made by means of a DuNouy tensiometer. For the more concentrated solutions equilibrium values were reached practically immediately after the surface was formed. However, for the more dilute solutions readings were taken over a period of time until constant values were obtained. Each time that measurements were made, several readings were taken and the results averaged.

Table 2. Typical raw data for dynamic surface tension measurements

(Santomerse D; Conc. 9.3529 g./l.; v_o = 233.0 cm./sec.; 25-26°C.; Picture series 163) (Data in cm.)

Plate no.	Line no.	Scale reading on measuring machine	Av. scale reading	Wave length
163a	Orifice	28.9602	28.9392	
		28.9182		
				1.0478
	1	27.8923		
		27.8900	27.8914	
		27.8918		
				1.0802
	2	26.8114		
		26.8110	26.8112	
		26.8112		
				1.1214
	3	25.6900		
		25.6895	25.6898	
		25.6898		
				1.1472
	4	24.5430		
		24.5424	24.5426	
		24.5425		
	5	23.3725		1.1687
		23.3732	23.3739	
		23.3760		
163b	3	26.0042		
		26.0030	26.0032	
		26.0025		
	4	24.8569		1.1470
		24.8554	24.8562	
		24.8562		
				1.1680
	5	23.6888		
		23.6880	23.6882	
		23.6878		
				1.1834
	6	22.5064		
		22.5045	22.5048	
		22.5036		
				1.1959

Table 2. (Continued)

Plate no.	Line no.	Scale reading on measuring machine	Av. scale reading	Wave length
	7	21.3085		
		21.3073	21.3089	
		21.3110		
	8	20.1037		1.2054
		20.1028	20.1035	
		20.1040		
163c	6	23.1557		
		23.1552	23.1551	
		23.1545		
	7	21.9642		1.1912
		21.9640	21.9639	
		21.9635		
				1.2050
	8	20.7601		
		20.7552	20.7589	
		20.7615		
				1.2172
	9	19.5419		
		19.5411	19.5417	
		19.5421		
	10	18.3216		1.2202
		18.3220	18.3215	
		18.3208		
163d	8	20.1467		
		20.1542	20.1489	
		20.1458		
				1.2186
	9	18.9273		
		18.9319	18.9303	
		18.9316		
				1.2190
	10	17.7131		
		17.7134	17.7113	
		17.7074		
	11	too dim to read		

The variation in readings for a single measurement was approximately ± 0.2 dyne per centimeter.

The tensiometer was calibrated by means of known weights over the range used in this study. The Harkins correction factors (31) for volume of liquid lifted by the ring were applied. Before each measurement the ring was cleaned by dipping it in hot chromic acid cleaning solution, rinsed with double distilled water and dried on clean filter paper.

Evaporation of water from the solutions between readings was a problem. It was reduced to a minimum by storing each solution in a closed space along with a container of water whose surface area was equal to or larger than the surface of the solution. Only a small amount of water was needed to saturate the air in the enclosed storage space and a large portion of it could come from the container of water rather than from the solution.

All measurements were made at 25 ± 2°C. Whenever the room temperature was outside this range, the solution was brought within this range immediately before the measurement by placing the watch glass containing the solution in contact with a beaker of water of the appropriate temperature.

Sinking time tests

The wetting ability of the solutions was measured by the canvas disc wetting test. The fabric used was Mount Vernon

Duck, #6, from Harrington, King and Co., Boston, Mass. Circles, one inch in diameter, were cut from the material with sharp shears so that the edges were not fuzzy.

Approximately 300 ml. of solution were used in a 400 ml. beaker. A 50-ml. beaker with several holes in the bottom was used to hold the fabric below the surface of the solution. Before the test the small beaker was brought to temperature in the solution. At the time of the test it was removed from the solution, the circle of fabric positioned in the bottom of the beaker and the beaker returned to the solution in an inverted position. A stop watch was started as the fabric entered the solution and stopped at the time the disc began to sink in the solution. The reading of the watch was recorded as the sinking time. The test was repeated using the same solution but a fresh disc each time until eight sinking times were obtained. Measurements showed considerable variation from the average.

All the sinking time tests were conducted at $25 \pm 2^{\circ}C$. When the room temperature was such that the solution in air was outside this range, the beaker containing the test solution was placed in a larger container of water whose temperature was controlled.

ADAPTATION OF THE VIBRATING JET METHOD TO THE DETERMINATION OF THE DEPENDENCE OF SURFACE TENSION ON TIME

Theoretical

Bohr (12) has shown that, for a jet issuing from an orifice of section $r = a + b \cos 2\theta$ with uniform velocity profile and constant surface tension,

$$\gamma = \frac{(\rho+\rho_m)v_0^2 k r_0^2 J_2(ikr_0)}{3 + k^2 r_0^2 i J_2'(ikr_0)} \left[1 + 2\left(\frac{2\mu}{\rho v_0^2 k r_0^2}\right)^{3/2} + 3\left(\frac{2\mu}{\rho v_0^2 k r_0^2}\right)^2\right] \cdot \left[1 + \frac{37b^2}{24a^2}\right] \qquad (1)$$

The meanings of the symbols in this equation and throughout the calculations are as follows:

γ = surface tension

ρ = density of the liquid

ρ_m = density of the surrounding medium

r_0 = radius of the orifice

v_0 = average velocity of the stream

$k = \frac{2\pi}{\lambda}$

J_2 = Bessel function of the second order

λ = wave length of wave at whose midpoint the surface tension is calculated
n = number of axes of symmetry
i = $\sqrt{-1}$
μ = viscosity
$\frac{b}{a}$ = $\frac{r_{max} - r_{min}}{r_{max} + r_{min}}$
a = radius of the stream
Q = volume rate of flow or discharge
$\frac{v}{v_o}$ = ratio of surface to bulk velocity
z = distance along jet measured from orifice

The assumption of constant velocity profile restricts the use of this equation to large distances from the orifice, but with this restriction the equation permits calculation of surface tension from observed wave length, mean velocity, and mean stream radius. Corrections for viscous damping and finite amplitude of the waves are included.

It is assumed that the flow of liquid through the orifice is lamellar, at least at the wall of the orifice. Hence, the axial velocity at the wall must be zero within the orifice, and the surface of the liquid immediately after issue from the orifice is therefore assumed to be new surface. If the velocity profile of the jet were constant, the mean velocity would also be the surface velocity and the surface age could be readily evaluated from the measured mean velocity v_0 and axial distance from the orifice z; thus

$$t = z/v_0 \, . \tag{2}$$

However, the surface velocity differs from the mean velocity; it is zero at the orifice and approaches v_0 only at large z. Surface ages evaluated by use of equation (2) are therefore unreliable in principle and are certain to be greatly in error for small ages (portions of the jet near the orifice) which are of particular interest. If the surface velocity were known as a function of time, then the axial distance from the orifice travelled by a surface element in time t could be obtained by integration,

$$z(t) = \int_0^t v(t)dt \, . \tag{3}$$

This relation could be used to evaluate an accurate surface age from an observed axial distance.

Basically, therefore, adaptation of the vibrating jet method to the determination of the dependence of surface tension on time involved three fundamental problems at the time this work was initiated, namely:

1. The basic equation, equation (1), for the calculation of surface tension from jet parameters was derived only for the case of constant surface tension; whether or

not important modification in its form resulted from a time dependent surface tension was unknown.

2. The dependence of surface velocity on axial distance was unknown, and, as a consequence, no sound method existed for the calculation of surface ages from axial distances from the orifice. It was presumed, both intuitively and from the work of Rideal and Sutherland (42), that the dependence of surface velocity on axial distance from the orifice would be influenced by orifice design.
3. The basic equation, equation (1), for the calculation of surface tension from jet parameters was derived for the case of uniform velocity profile and the effect on its form of the non-uniform velocity profile in the jet region of particular interest (near the orifice) was unknown.

The first of these problems was investigated by Hansen (28) for the uniform velocity profile case. He assumed that the surface tension varied linearly with time over one wave length, treated the variation as a perturbation, and solved the resulting problem by successive approximations. He was able to show that, to good approximation, equation (1) gave the mean surface tension over the measured wave length. A small correction due to variation in jet radius could be omitted if actual jet radius at the point of measurement, rather than the orifice radius, was used in the calculation.

The second of these problems was solved by Hansen and Wallace (30). Bohr (12) had given a general form for the velocity profile in the jet in terms of a Fourier-Bessel series in r, the radial distance, and t, the time after leaving the orifice. Schiller (47) had studied the flow of liquids in pipes and, using Prandtl boundary layer approximation, derived an approximate velocity profile within the pipe in terms of distance from the entrance, tube radius, and Reynold's number. Schiller was able to prove experimentally that the velocity profile thus derived accounted for observed liquid flow properties through the pipe with great precision. Hansen and Wallace therefore used Schiller's velocity profile (established in terms of orifice length), the radius, and the Reynold's number of liquid flowing through the orifice to furnish an initial boundary condition on Bohr's Fourier-Bessel series and thereby were able to determine the coefficients in the series. They then evaluated the series for $r = r_0$, the jet radius, repeating the evaluation for a sufficient number of orifice flow conditions to permit interpolation. The surface velocity having thus been established as a function of time, the axial distance travelled by a surface element in time t was obtained by integration. The determination of surface age was thus permitted from measured axial distance. They then used the relation between surface age and axial distance to establish the dependence of surface velocity on axial distance.

The dependence of surface velocity on axial distance according to these calculation is shown in Figure 9. Ordinate and abscissa are dimensionless groups proportional to surface velocity and axial distance; the parameter r'/r_o is the ratio of the radius of the flat portion of the velocity profile to the tube radius. The dependence of this ratio, as given by Schiller, on orifice length, radius, and Reynold's number is given in Figure 10. The dependence of surface age on axial distance for the jet used in the present work will be presented later.

The third problem, the effect of the non-uniform velocity profile on the form of equation (1) presents a problem in hydrodynamics which does not appear solvable mathematically by present techniques of mathematical hydrodynamics. Since the velocity profile was known and the wave lengths could be measured, it was therefore decided to attempt an experimental solution of this problem using liquids of constant, known surface tensions and relying on the principle of similitude.

In a jet with mean velocity v_o issuing from an orifice whose section is $r = a + b \cos 2\theta$ waves are observed in the jet of wave number k. The wave number may be expected to depend on the surface tension of the liquid (γ), its density (ρ) and viscosity (μ), on its mean velocity (v_o), on the parameters of

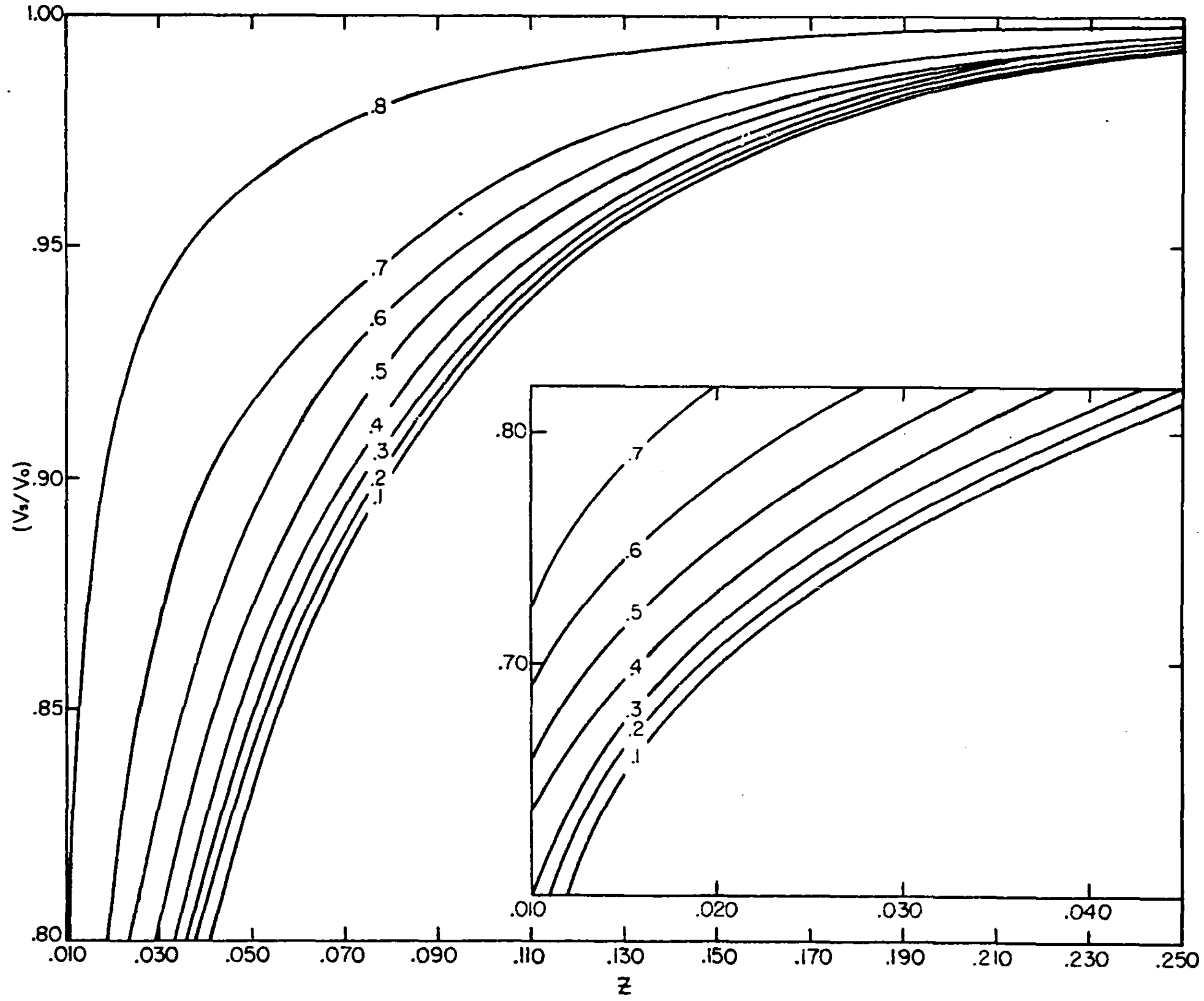


Figure 9. Dependence of ratio of surface to bulk velocity on Z

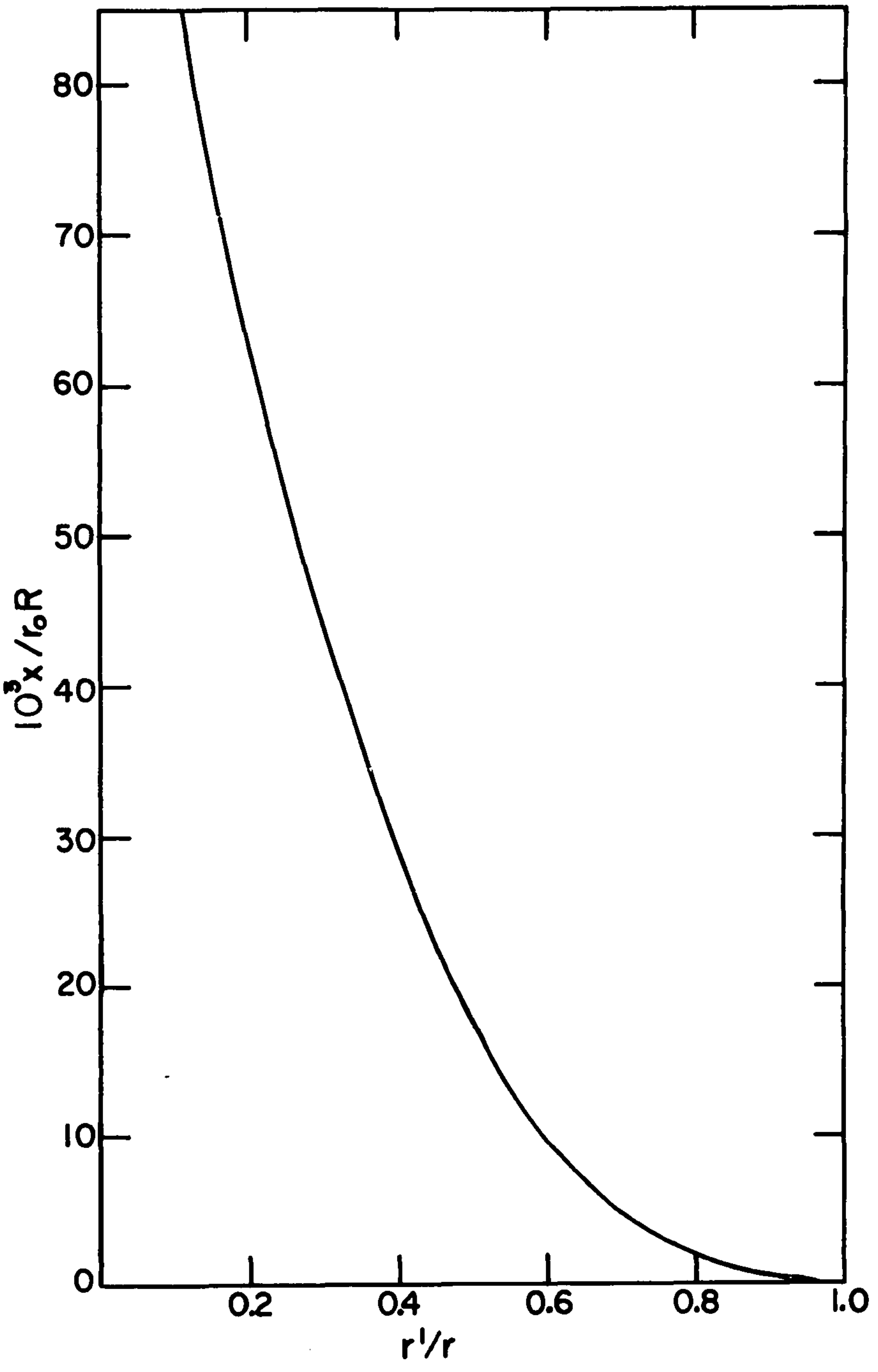


Figure 10. Dependence of r'/r on x/r_oR

the jet orifice (a and b), and on the velocity profile. The velocity profile may be tentatively characterized by the ratio of surface to mean velocity, that is, by v/v_0, with the reservation that this single ratio may be inadequate for the characterization. Then the statement of the variables on which the wave number depends implies the functional relationship

$$F\,(k,\ \gamma\ ,\ \rho\ ,\ \mu\ ,\ v_0, a,\ b,\ v/v_0)\ =\ 0\,. \qquad (4)$$

There are three independent dimensions involved in the eight functionally related variables; the principle of similitude (36b) requires that the functional dependence among the eight variables be reducible to a functional relationship among five dimensionless groups, choice of which is immaterial so long as they are independent. With the choice of dimensionless groups suggested by the form of equation (1), equation (4) must therefore reduce to

$$G\left(\frac{\gamma}{\rho\, v_0{}^2 a},\ ka,\ \frac{2\,\mu}{\rho\, v_0{}^2 k\ a^2},\ b/a,\ v/v_0\right)\ =\ 0 \qquad (5)$$

Furthermore, equation (5) must reduce to equation (1) when $v/v_0 = 1$.

Equation (5) permits one variable, say $\frac{\gamma}{\rho\, v_0{}^2 a}$, to be expressed as a function of the remaining four and in principle this function can be determined experimentally and tabulated. The work required would, of course, be formidable, although much less than would be required for seven independent variables, as suggested by equation (4).

It was therefore decided to test equation (5) for separability of the functional dependence on v/v_0. Equation (1) is of the form

$$\frac{\gamma}{\rho v_0^2 a} = f\left(ka, \frac{2\mu}{\rho v_0^2 k a^2}, \frac{b}{a}\right) \tag{6}$$

and is valid if $v/v_0 = 1$. The assumption of separability implies that

$$\frac{\gamma}{\rho v_0^2 a} = f\left(ka, \frac{2\mu}{\rho v_0^2 k a^2}, \frac{b}{a}\right) g\,(v/v_0) \tag{7}$$

when $v/v_0 \neq 1$ and where f is the same function in equations (6) and (7) and is in fact completely implied by equation (1). Furthermore, the form of $g\,(v/v_0)$ is limited by the requirement that $g\,(1) = 1$. A trial function of the form $g\,(v/v_0) = (v/v_0)^m$ was selected as one of many possessing this property. Equation (7) can then be rearranged to

$$\gamma = \gamma_{app}\,(v/v_0)^m \tag{8}$$

in which γ_{app} is the apparent surface tension calculated from equation (1) and the quantity $(v/v_0)^m$ serves as a correction factor. The validity or lack of validity of equation (8) can be demonstrated experimentally by measuring properties of jets formed by liquids with different velocities, velocity profiles, densities, surface tensions and viscosities issuing from various orifices, and alternate assumptions can be made if necessary.

A somewhat modified form of equation (1) was used in actual calculations. This was obtained by neglecting ρ_m (density of air), substituting $Q/\pi a^2$ for v_0 in the leading term, setting $n = 2$, setting $k = 2\pi/\lambda$, and expanding the ratio of Bessel functions

$$\frac{J_2(ika)}{ika\ J_2'(ika)}$$

in power series in ka to the three leading terms. There results

$$\gamma_{app} = \frac{2\rho Q^2}{3a\lambda^2}\left\{1 - \frac{5\pi^2 a^2}{3\lambda^2} + .85\left[\frac{5\pi^2 a^2}{3\lambda^2}\right]^2\right\}\left\{1 + \frac{37\ b^2}{24\ a^2}\right\}.$$

$$\left\{1 + 2\left[\frac{\mu\lambda}{\pi\rho\ v_0 a^2}\right]^{3/2} + 3\left[\frac{\mu\lambda}{\pi\rho\ v_0 a^2}\right]^2\right\} \qquad (9)$$

The force of gravity serves to impart a downward acceleration to each element in the jet stream. A jet issuing horizontally therefore curves downward and the curvature interferes with the focusing of light by the jet and makes interpretation of spacing of lines focused on a photographic plate in terms of jet wave length difficult. Therefore, a vertical jet was used in the present work; that is, the jet issued downward from the orifice. The linear velocity therefore increased (due to gravity) with axial distance from the orifice, and since the volume flow rate Q must be independent of axial distance, the stream radius decreased with axial distance. If z is the axial distance from the orifice, v_z is the velocity at z and v_e the velocity at efflux, then

$$v_z = v_e\left(1 + \frac{2gz}{v_e}\right)^{\frac{1}{2}} \tag{10}$$

Since $Q = \pi a^2 v$ is constant, if a_z is the stream radius at z and a_o the stream radius at efflux, then

$$a_z = a_o\left(1 + \frac{2gz}{v_o}\right)^{-\frac{1}{4}} \tag{11}$$

This amounted to a small but not negligible correction to the leading term in equation (9); the effect of this variation on higher order terms was negligible and was ignored.

When a jet issues from an orifice there is a contraction of the radius, the magnitude of which depends on the orifice design. A minimum radius is reached at a distance of the order of a few diameters from the orifice and this is known as the vena contracta. Because of this, a_0 was calculated from measurements on the jet below the vena contracta and was not simply taken from the orifice. In jets observed a_0 was from two to four percent less than the orifice radius.

Experimental

Equation (9) was tested experimentally by studying the variation in wave length with distance for jets of water, acetone, and butyl alcohol, using two jet velocities in each case. These liquids cover a range of surface tensions from 23.3 to 72 dynes/cm. and of viscosities from 3.15×10^{-3} to 2.52×10^{-2} poises.

Jet wave lengths were determined as the differences between the average positions of the lines on the photographic plates. These differences were plotted and a smooth curve drawn through the points. Figure 11 is an example of such a plot. Wave lengths as determined from the graph were used in the calculation of surface tension. Because of the uncertainty of the position of the orifice and because the distance from the orifice to the first line was not always a full wave, the first wave length was not used in calculating surface tension but it was used in determining the distance of the midpoint of each

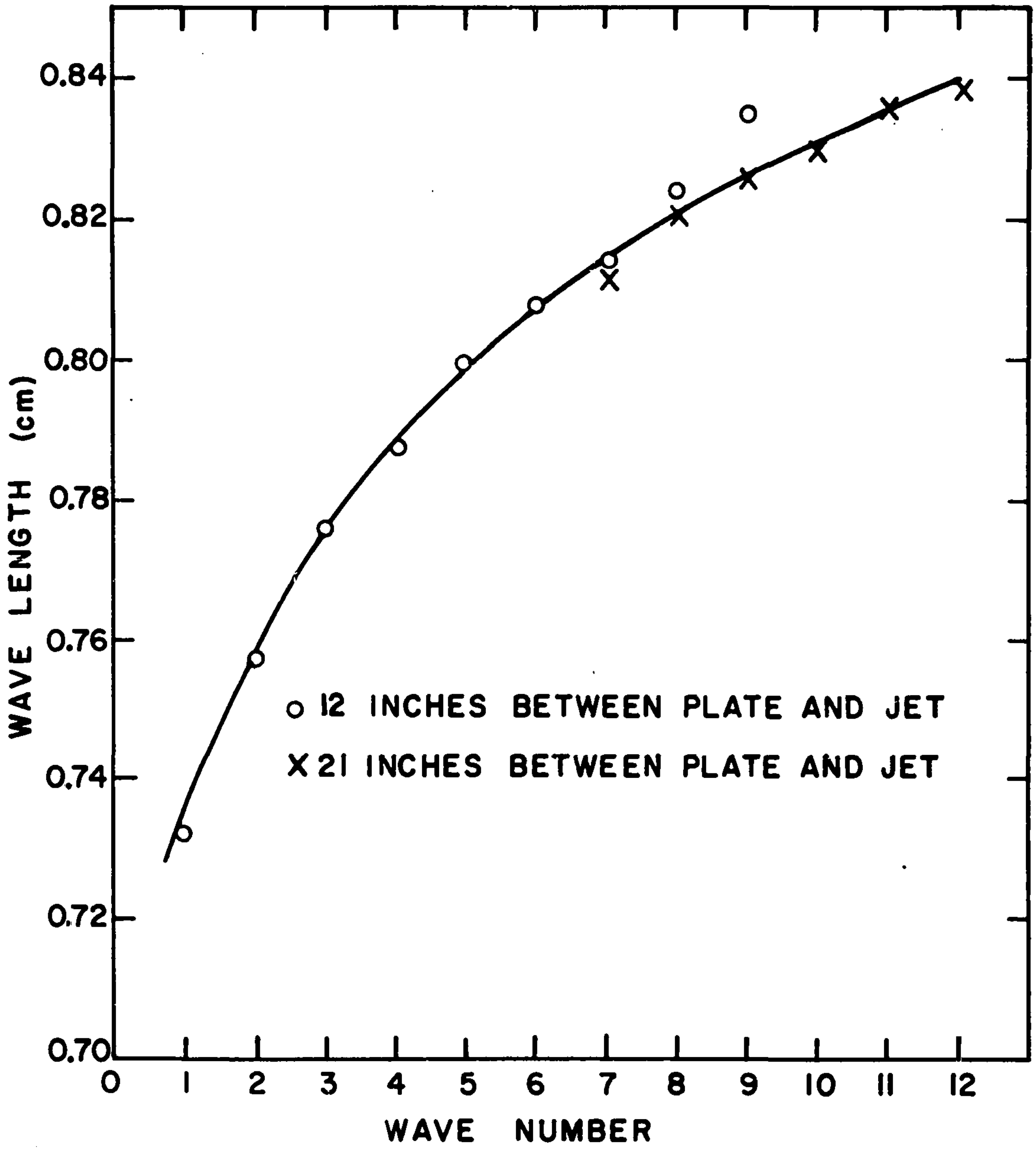


Figure 11. Wavelengths from photographs of water jets

wave from the orifice. The uncertainty or error in position of the orifice was unimportant for this use.

The velocity of the stream was obtained from the relationship between linear velocity, diameter, and volume rate of flow or discharge.

$$v = \frac{4Q}{\pi d^2} = \frac{Q}{\pi a^2} \tag{12}$$

The diameter of the stream was obtained from measurements on the picture of the stream photographed with the real camera. The exact magnification in the picture was obtained by comparison of the diameter of a glass rod in the picture with the actual measurements of the rod. The diameters of the stream in the neighborhood of the maximum and minimum were measured and the values divided by the magnification factor to obtain the diameters of the stream itself. An equal number of values at the maximum and minimum were averaged and this figure was considered to be the diameter at a point half way between the maximum and minimum.

Stream radius at the midpoint of each wave was corrected for the acceleration of gravity as previously explained (equations 10 and 11). Viscosities and densities were taken from Lange's Handbook of Chemistry. These data complete the requirements for calculation of γ_{app} from equation (9).

True surface tensions of water, acetone and butanol were taken from the International Critical Tables as 72.0, 23.3, and 24.1 dynes/cm., respectively, at the temperature used in the test. Hence, in order to test equation (8) the only remaining undetermined physical quantity is the ratio of the surface to mean velocity, v/v_o. The results of Hansen and Wallace (30) permit this ratio to be evaluated from orifice length, diameter, and flow Reynold's number. Since the orifice used had a tapered entrance, there was some uncertainty as to its effective length. The actual straight section of the orifice was approximately 0.2 cm., but this section was preceded by a five-centimeter section tapering from 0.6 to 0.1 cm. in diameter. Initially, calculations were made on the assumption that the orifice was equivalent to a one-centimeter straight section connected to an infinite reservoir. Results were sufficiently encouraging that work was initiated by Hansen and Wallace on straight orifices of measured lengths; their results indicated that the orifice used in the present work was equivalent to a 0.5 cm. straight section connected to an infinite reservoir. Results were recalculated on this basis.

The value of v/v_o corresponding to a given axial distance was calculated in the following manner: the value of x, equivalent straight section of the orifice, was taken as 0.5 cm. as previously explained; the orifice radius a was 0.0532 cm.; the Reynold's number, $R = \rho v_o a/\mu$, was calculated from measured mean velocity in the orifice, $v_o = Q/\pi a^2$. Hence, the quantity x/aR was obtained and the ratio of radius of flat section of velocity profile at efflux to orifice radius, r'/r_o, was obtained from Schiller's graph, Figure 10. Dependence of v/v_o on axial distance for various values of r'/r_o was available from the work of Hansen and Wallace as shown in Figure 9; hence, this ratio could be obtained for measured axial distance for the known value of r'/r_o by interpolation between curves for values of this parameter used in their calculation.

Plots of log (γ/γ_{app}) against log (v/v_o) should be linear according to equation (8). Linear plots were, in fact, obtained. A composite value of the slope obtained from the present work and the work of Wallace was 0.62. These results, therefore, support equation (8) in the form

$$\gamma = \gamma_{app}(v/v_o)^{0.62} \qquad (12)$$

The difference between γ and γ_{app} is about 20% for the initial waves for water and aqueous solutions.

The following example illustrates the steps involved in calculating surface tensions. Data for water are used in this case.

ρ = 0.997 g/cm.^{3}

μ = 0.00894 poises

a_o = 0.05218 cm.

$$r = 0.0532 \text{ cm.}$$

$$Q = 1.993 \text{ cm.}^3/\text{sec.}$$

$$v_o = \frac{Q}{\pi a^2} = \frac{1.993}{\pi(.05218)^2} = 233.0 \text{ cm./sec.}$$

$$R = \frac{\rho v_o r}{\mu} = \frac{0.997\ (233.0)\ (0.0532)}{0.00894} = 1330$$

$$x = 0.5 \text{ cm.}$$

$$\frac{x}{Rr} = \frac{0.5}{1330\ (0.0532)} = 7.07 \times 10^{-3}$$

The value of x/Rr was used with Schiller's graph, Figure 10, to obtain $r'/r = 0.65$.

z = the distance from the orifice to the midpoint of the specified wave

$$Z = \frac{z\mu}{v_o \rho a_o^2} = 14.1 \times 10^{-3} z$$

Values of v/v_o were obtained from the graph by Hansen and Wallace, Figure 9. Values of a were read from a graph of a vs. z for the given velocity. Points on this graph were located by means of equation (10) and (11).

$$c_1 = 1 - \frac{5\pi^2 a^2}{3\lambda_m^2} + 0.85\left[\frac{5\pi^2 a^2}{3\lambda_m^2}\right]^2$$

$$c_2 = 1 + \frac{37b^2}{24a^2}$$

The ratio b/a decreases as the waves damp out. This effect was calculated from the equation given by Bohr (12, p. 298).

$$b/a = (b/a)_0 \, e^{-\epsilon z}$$

where $\epsilon = \frac{4\mu}{\rho v a^2}$.

$$c_3 = 1 + 2\left[\frac{\mu\lambda}{\pi\rho \, v_0 a^2}\right]^{3/2} + 3\left[\frac{\mu\lambda}{\pi\rho v_0 a^2}\right]^2$$

Typical data used in calculating surface tensions are presented in Table 3; data for water are used in this case.

Values of surface tensions of water, acetone, and butanol calculated by means of equation (12) for various flow rates and axial distances are presented in Table 4. Except for the surface tension from the first wave all the values obtained for the surface tension of water at a velocity of 233.0 cm./sec. are within 0.5 dyne/cm. of the accepted value, 72.0 dynes/cm. at 25°C. Although the values are slightly less constant for the surface tension of water at the lower velocity, there is no steady trend to higher or lower values. Furthermore, only three of the values are more than one dyne/cm. different from the accepted value.

At a velocity of 252.6 cm./sec. the values obtained for the surface tension of acetone are slightly lower than the accepted value, 23.3 dynes/cm. at 22-23°C. However, except for the first two waves the values are constant and very close to the accepted value. The data for butanol also show the constancy of the surface tension along the jet and the

Table 3. Typical data used in calculating surface tensions

(Water, 25°C, $Q = 1.993$ cm.^{3}/sec.)

Wave No.	λ cm.	z cm.	$Z =$ $14.1\,z$	a $\times 10^2$ cm.	$\left[\frac{v}{v_o}\right]^{.62}$	c_1	c_2	c_3	γ dynes/cm.
1	0.731	0.366	---	---	---	---	---	---	---
2	0.755	1.109	15.64	5.170	0.851	0.930	1.0009	1.0004	71.16
3	0.744	1.873	26.41	5.137	0.888	0.933	1.0009	1.0004	71.59
4	0.788	2.654	37.42	5.100	0.918	0.935	1.0008	1.0004	71.84
5	0.800	3.448	48.62	5.068	0.936	0.937	1.0007	1.0004	71.65
6	0.808	4.252	59.95	5.038	0.948	0.940	1.0007	1.0004	71.90
7	0.815	5.064	71.40	5.003	0.957	0.941	1.0006	1.0004	71.76
8	0.821	5.881	82.92	4.973	0.965	0.943	1.0006	1.0004	71.88
9	0.827	6.706	94.55	4.943	0.971	0.944	1.0005	1.0004	72.03
10	0.832	7.535	106.24	4.913	0.976	0.945	1.0005	1.0004	71.91
11	0.837	8.369	118.00	4.885	0.980	0.946	1.0004	1.0004	71.90
12	0.840	9.208	129.83	4.855	0.983	0.947	1.0004	1.0004	71.92

Table 4. Surface tension of pure liquids

(Data in dynes/cm.)

Wave No.	Vel. (cm./sec.)						
	Water		Acetone		Butanol		
	233.0	187.1	252.6	218.6	204.9	170.5	170.5
2	71.2	73.3	21.5	23.7	23.6	23.4	24.8
3	71.6	73.1	22.3	23.5	24.6	24.4	25.0
4	71.8	72.7	22.8	24.1	24.7	24.6	24.9
5	71.6	72.1	22.9	23.7	24.5	24.4	24.7
6	71.9	71.7	22.8	23.4	24.5	24.3	24.6
7	71.8	71.8	22.7	23.4	24.3	24.1	24.6
8	71.9	71.7				23.9	
9	72.0	71.5					
10	71.9	70.9					
11	71.9	71.4					
12	71.9	71.5					
13	72.5						
14	72.5						
15	72.5						

values obtained are all close to the accepted value of 24.1 dynes/cm. at 25°C.

Determination of Surface Age

The dependence of surface age on axial distance for various values of the parameter r'/r_0 had been established by Hansen and Wallace in terms of $\tau - Z$ and Z, where $\tau = \frac{\mu t}{\rho r_0^2}$ and $Z = \frac{\mu z}{v_0 \rho r_0^2}$. Since the same orifice and essentially the same discharge rate were used in all experiments with detergent solutions, the value of r'/r_0 was the same for all experiments.

Table 5 gives the values of $\tau - Z$ and Z as obtained by interpolation from the data of Hansen and Wallace. In the same table the corresponding values of z, axial distance, and t, the surface age, are given. Figure 12 is based on the t vs. z data from Table 5.

Since each surface element travels an additional distance $\frac{1}{2}gt^2$ in time t due to the acceleration of gravity, a correction for this acceleration was made. The corrected curve is also shown in Figure 12.

Table 5. Data for obtaining age of surface from distance along stream

z cm.	Z^a x 10^2	$\frac{r'}{r_0} = 0.6$			$\frac{r'}{r_0} = 0.7$		
		$\tau^b - Z$	τ	t sec.	$\tau - Z$	τ	t sec.
1.0	1.412	0.0108	0.0249	0.00757	0.0092	0.0233	0.00708
2.0	2.824	0.0151	0.0433	0.01316	0.0122	0.0404	0.01228
3.0	4.236	0.0176	0.0600	0.01824	0.0142	0.0566	0.01721
4.0	5.648	0.0194	0.0759	0.02307	0.0156	0.0721	0.02192
5.0	7.060	0.0208	0.0914	0.02778	0.0168	0.0874	0.02657
6.0	8.472	0.0218	0.1065	0.03238	0.0176	0.1023	0.03110
7.0	9.884	0.0226	0.1214	0.03691	0.0182	0.1170	0.03557
8.0	11.296	0.0232	0.1362	0.04141	0.0186	0.1316	0.04001
9.0	12.708	0.0237	0.1508	0.04584	0.0190	0.1461	0.04441
10.0	14.120	0.0240	0.1652	0.05022	0.0194	0.1606	0.04882

[a] $Z = \frac{\mu z}{v_0 r_0^2 \rho}$.

[b] $\tau = \frac{\mu t}{\rho r_0^2}$.

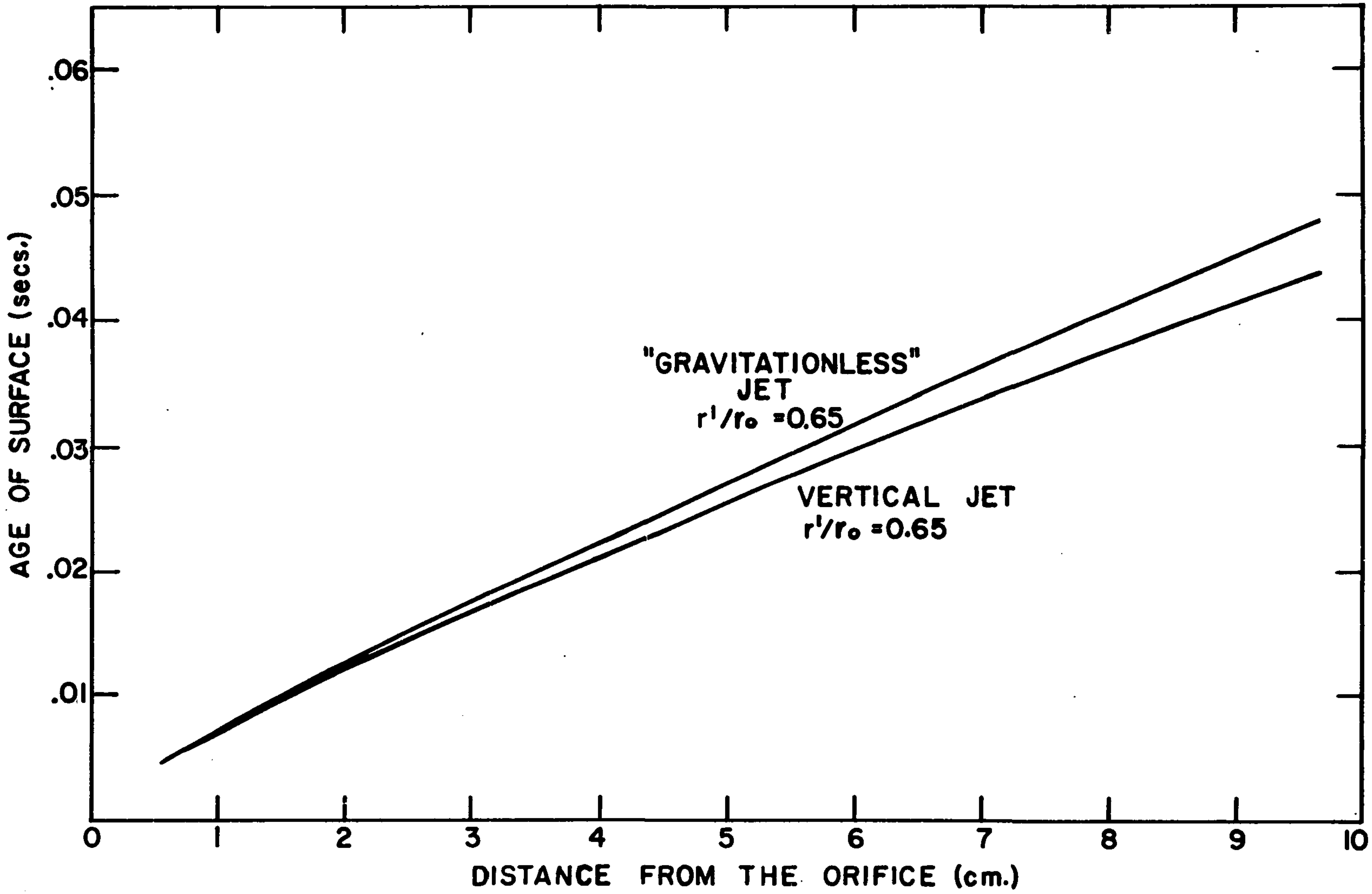


Figure 12. Dependence of age of the surface of the jet on distance from the orifice

RESULTS

Dynamic Surface Tensions

The dependence of surface tension on time was measured for five solutions of Areskap 100, the concentration of the solutions covering the range from 0.325 to 5.197 grams/liter. The results are presented in Table 6 and Figure 13.

The dynamic surface tensions of six solutions of Santomerse D are presented in Table 7 and Figure 14. The concentration range was from 0.292 to 9.353 grams/liter.

The relationships between surface tension and time for trimethyldodecylammonium chloride solutions are given in Table 8 and Figure 15. The four solutions studied ranged in concentration from 1.066 to 4.320 grams/liter.

Equilibrium Surface Tensions

Dependence of equilibrium surface tension on concentration in aqueous solutions of Areskap, Santomerse D and trimethyldodecylammonium chloride is presented in Table 9 for concentration ranges of interest for the dynamic surface tension studies.

Table 6. Dynamic surface tensions: Areskap 100

(v_0 = 233.0 cm./sec.)

Wave no.	Concentration								
	0.3248 g./l.			0.6496 g./l.			1.2992 g./l.		
	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t\text{x}10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t\text{x}10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t\text{x}10^2$ sec.
0	(.70)	---	---	(.63)	---	---	(.65)	---	---
1	.751	71.4	.75	.758	69.8	.70	.780	66.3	.72
2	.769	72.4	1.13	.780	69.2	1.10	.824	62.9	1.13
3	.783	72.6	1.52	.800	69.6	1.50	.864	60.2	1.55
4	.796	72.2	1.87	.817	68.8	1.85	.896	58.0	1.95
5	.806	72.1	2.24	.833	68.2	2.25	.922	56.4	2.35
6	.813	72.1	2.57	.846	66.9	2.60	.945	55.1	2.74
7	.820	72.0	2.92	.858	66.1	2.93	.962	53.7	3.13
8	.826	71.9	3.24	.868	65.5	3.28	.978	52.7	3.52
9	.832	71.8	3.55	.878	64.9	3.62	.994	51.8	3.87
10	.836	72.0	3.87	.888	64.2	3.94	1.100	50.7	4.25
11	.840	71.9	4.18						
12	.845	71.8	4.50						
13	.849	71.7	4.82						

Table 6. (Continued)

Wave no.	Concentration					
	2.5985 g./l.			5.1970 g./l.		
	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t \times 10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t \times 10^2$ sec.
0	(.87)	---	---	(.84)	---	---
1	.862	56.4	.86	.964	45.6	.87
2	.930	51.5	1.30	1.026	43.0	1.36
3	.975	48.8	1.75	1.071	41.0	1.85
4	1.006	47.2	2.20	1.098	40.1	2.34
5	1.034	45.7	2.64	1.122	39.2	2.80
6	1.054	44.8	3.06	1.139	38.9	3.25
7	1.072	44.0	3.45	1.153	38.5	3.69
8	1.086	43.6	3.87	1.167	38.2	4.12
9	1.098	43.2	4.30	1.180	37.8	4.57
10	1.110	42.8	4.71	1.192	37.5	4.98

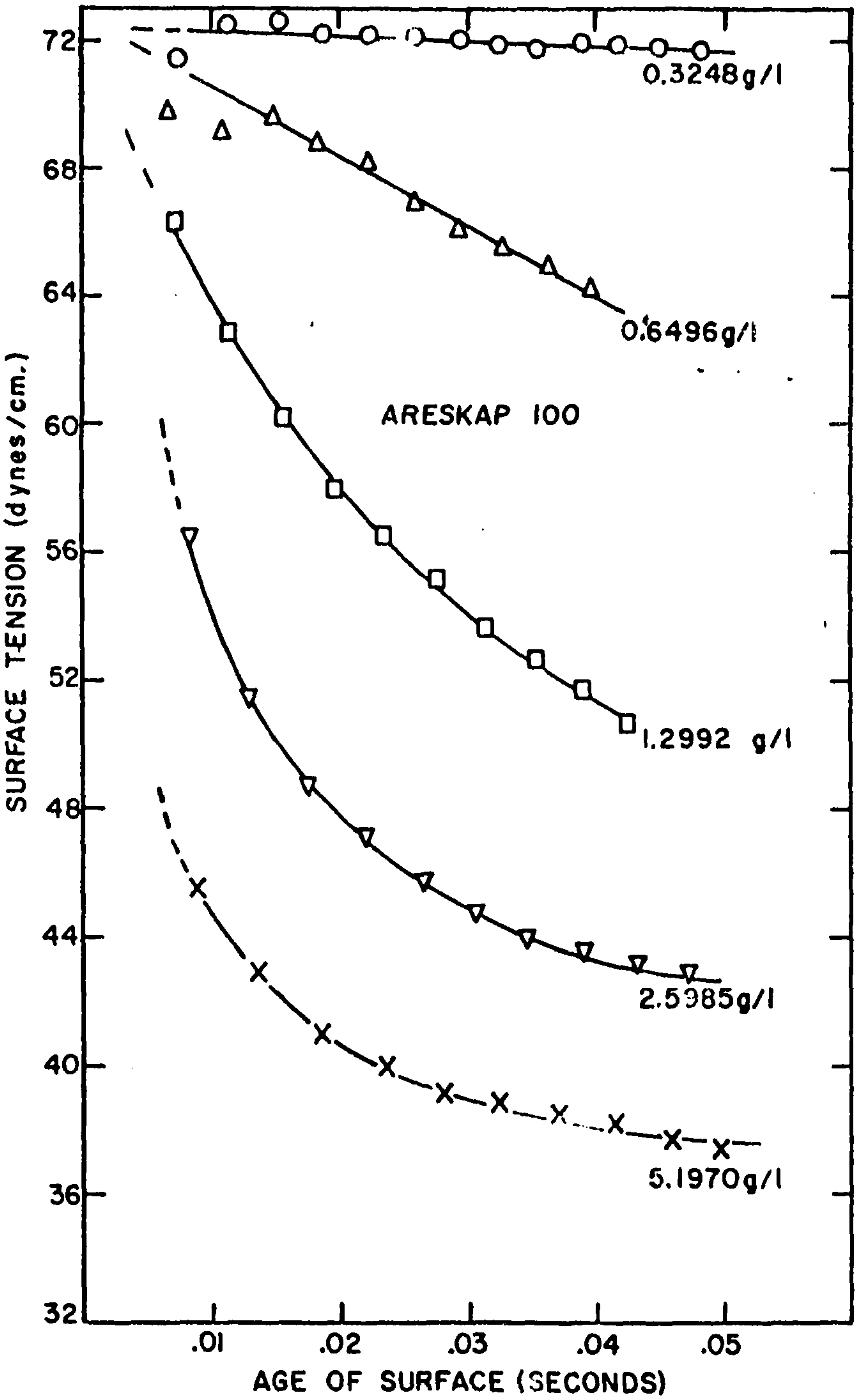


Figure 13. Dependence of surface tension of Areskap 100 solutions on time

Table 7. Dynamic surface tensions: Santomerse D

(v_0 = 233.0 cm./sec.)

Wave no.	Concentration								
	0.2923 g./l.			0.5846 g./l.			1.1691 g./l.		
	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$tx10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$tx10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$tx10^2$ sec.
0	(.69)	---	---	(.67)	---	---	(.66)	---	---
1	.755	70.8	0.74	.762	69.3	0.73	.818	60.9	0.73
2	.778	71.2	1.13	.787	69.4	1.13	.863	59.2	1.17
3	.790	71.4	1.52	.809	68.3	1.52	.896	56.7	1.59
4	.800	71.6	1.88	.828	67.2	1.88	.921	55.2	2.02
5	.809	71.5	2.25	.843	66.2	2.28	.940	54.4	2.42
6	.817	71.5	2.58	.853	66.1	2.63	.954	53.8	2.81
7	.825	71.2	2.92	.862	65.7	2.97	.967	53.2	3.20
8	.831	71.2	3.25	.871	65.2	3.32	.978	52.8	3.57
9	.837	71.1	3.56	.879	64.9	3.64			
10	.843	70.8	3.88	.889	64.5	3.98			
11	.847	70.8	4.21						

Table 7. (Continued)

Wave no.	Concentration								
	2.3382 g./l.			4.6764 g./l.			9.3529 g./l.		
	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t \times 10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t \times 10^2$ sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	$t \times 10^2$ sec.
0	(.77)	---	---	(.87)	---	---	(.54)	---	---
1	.938	47.8	0.84	1.035	40.0	0.89	1.080	37.5	1.00
2	.992	45.5	1.30	1.085	38.7	1.43	1.121	36.7	1.54
3	1.029	44.3	1.79	1.117	38.1	1.93	1.147	36.4	2.07
4	1.055	43.2	2.26	1.138	37.7	2.44	1.167	36.2	2.56
5	1.074	42.6	2.70	1.152	37.4	2.92	1.183	35.7	3.04
6	1.092	41.9	3.14	1.164	37.4	3.37	1.196	35.8	3.52
7	1.109	41.5	3.56	1.176	37.4	3.81	1.205	35.7	3.95
8	1.124	40.9	3.97	1.187	37.2	4.25	1.214	35.7	4.42
9	1.139	40.5	4.41	1.198	36.9	4.68	1.222	35.6	4.86

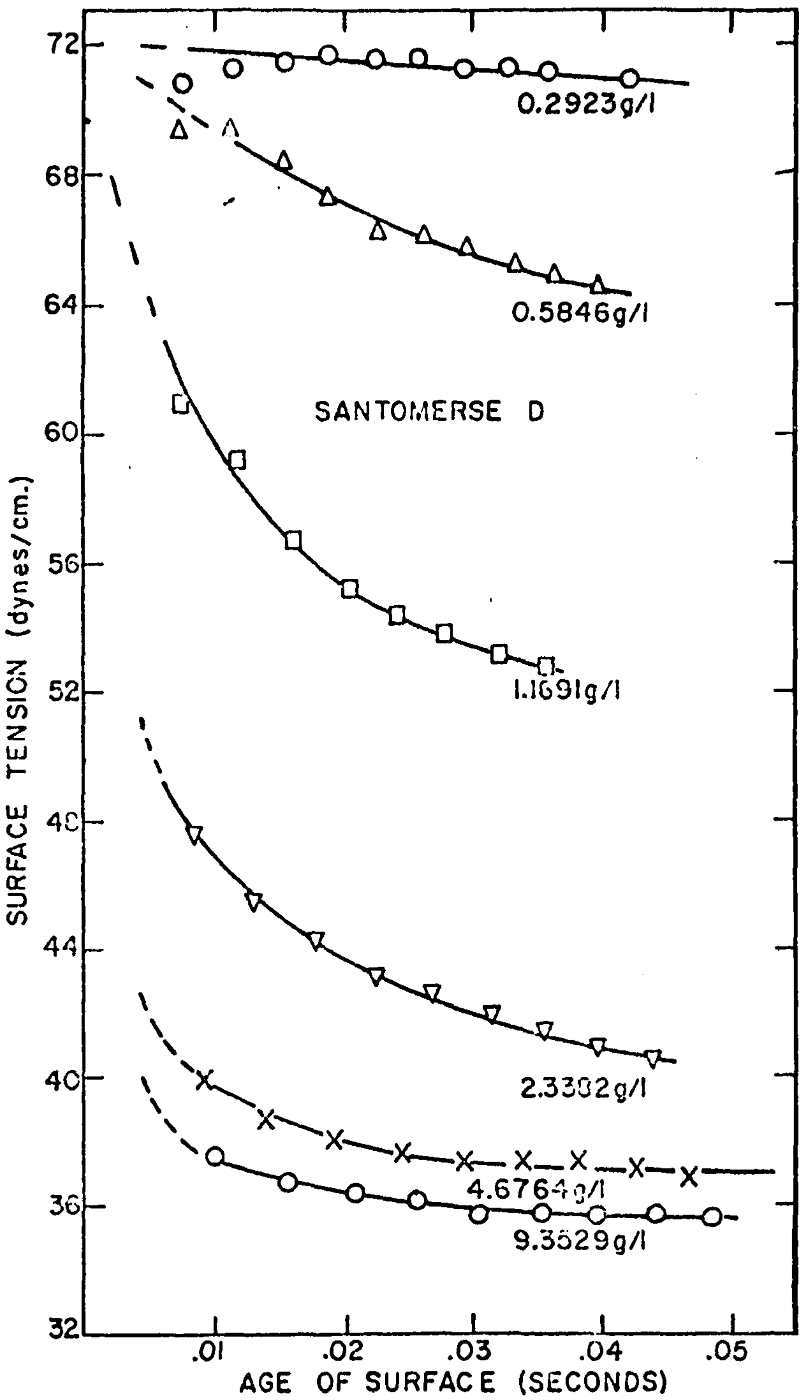


Figure 14. Dependence of surface tension of Santomerse D solutions on time

Table 8. Dynamic surface tensions: trimethyldodecylammonium chloride

(v_o = 233.0 cm./sec.)

Wave no.	Concentration					
	1.0663 g./l.			2.1601 g./l.		
	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	tx10^2 sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	tx10^2 sec.
0	(.34)	---	---	(.79)	---	---
1	.788	62.6	.52	.842	58.4	.83
2	.807	64.2	.97	.871	58.0	1.24
3	.823	65.4	1.38	.887	58.0	1.67
4	.836	65.4	1.76	.901	57.8	2.07
5	.848	65.2	2.16	.912	57.7	2.46
6	.859	64.7	2.55	.922	57.4	2.84
7	.867	64.7	2.88	.929	57.5	3.21
8	.875	64.4	3.23	.936	57.5	3.57
9	.882	64.4	3.55	.942	57.4	3.91
10	.886	64.5	3.88	.947	57.5	4.29
11	.894	64.0	4.23			
12	.894	64.7	4.56			

Table 8. (Continued)

Wave no.	Concentration					
	3.0466 g./l.			4.3202 g./l.		
	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	tx10^2 sec.	λ cm.	γ $\frac{\text{dynes}}{\text{cm.}}$	tx10^2 sec.
0	(.42)	---	---	(.84)	---	---
1	.884	52.2	.61	.931	48.4	.70
2	.902	53.4	1.09	.953	49.2	1.32
3	.917	53.9	1.53	.972	49.3	1.78
4	.932	53.9	1.96	.986	49.1	2.23
5	.944	53.8	2.39	.997	49.0	2.64
6	.955	53.4	2.77	1.006	49.0	3.05
7	.965	53.3	3.17	1.014	49.0	3.44
8	.974	53.2	3.54	1.021	49.0	3.83
9	.982	52.9	3.89	1.028	49.0	4.22
10	.990	52.7	4.27	1.031	49.3	4.60
11	.997	52.6	4.63			

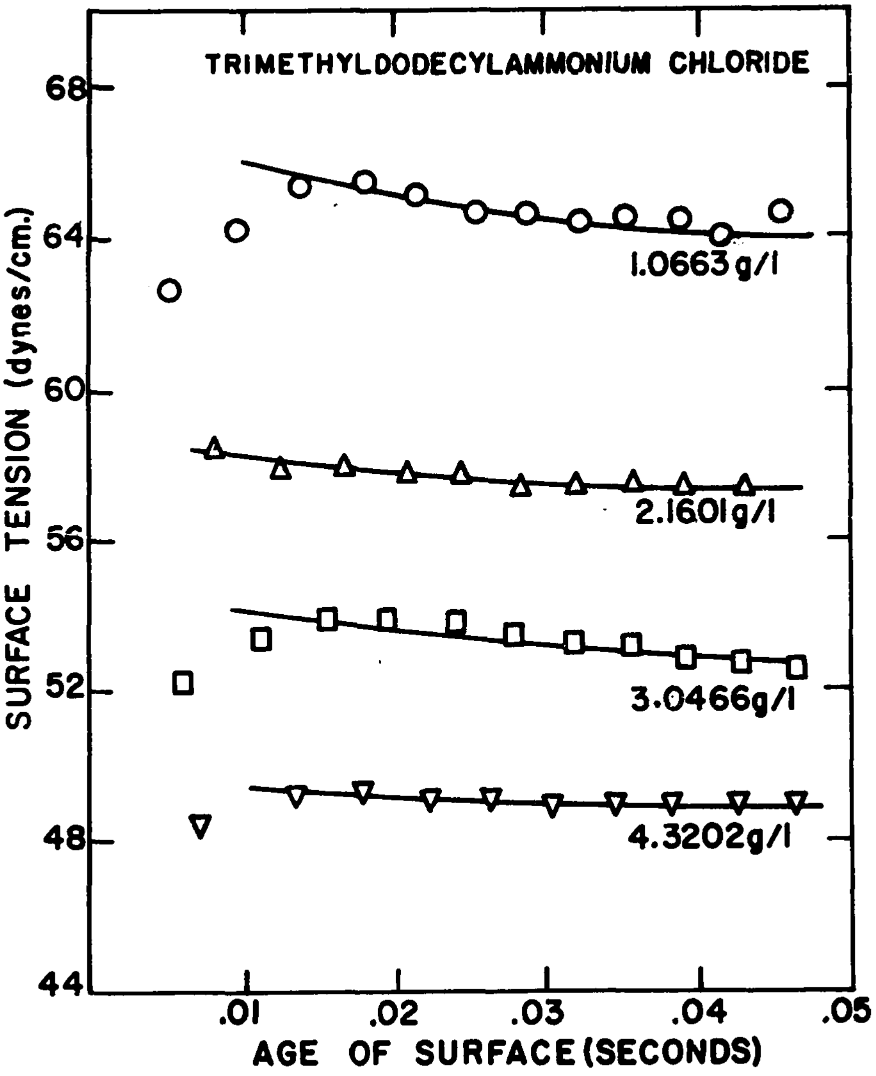


Figure 15. Dependence of surface tension of trimethyldodecylammonium chloride solutions on time

Table 9. Equilibrium surface tensions

Surface active material	Conc. g./l.	Equilibrium surface tension dynes/cm.	Comments
Areskap	5.1970	31.9	Constant for 2 days
	2.5985	31.9	Constant for 2 days
	1.2992	31.2	Constant for 2 days
	0.6495	31.4	Over period of 6 days dropped from 33.9, constant for 3 days
	0.3248	34.0	Over period of 3 days dropped from 35.6, constant for 1 day
Santomerse D	9.3529	33.0	
	4.6764	33.0	Constant over 3 days
	2.3382	32.0	Constant over 3 days
	1.1691	29.5	Over period of 3 days dropped from 30, constant for 2 days
	0.5846	29.0	Over period of 5 days dropped from 33, dropped 1 dyne/cm. in last 2 days
	0.2923	32.2	Over 3 days dropped from 37.6

Table 9. (Continued)

Surface active material	Conc. g./l.	Equilibrium surface tension dynes/cm.	Comments
Trimethyl-dodecyl ammonium chloride	4.3202	34.5	Average of readings from 16-40 hours; range 1.6 dynes/cm.
	3.588	36.4	Average of readings from 16-24 hours; range, 1.5
	2.1326	37.2	Average of 7 readings; range, 1 dyne/cm.
	1.0663	40.6	Average of reading from 16-24 hours; range less than 1 dyne/cm.

Wetting Times

Dependence of canvas disc wetting times on concentration for aqueous solutions of Areskap 100, Santomerse D, and trimethyldodecylammonium chloride is presented in Table 10 and Figure 16.

Table 10. Wetting times for solutions studied

Surface active agent	Concentration g./l.	Wetting time sec.	Standard deviation[a] sec.
Areskap 100	0.3248	397.8	18.0
	0.6496	86.8	19.0
	1.2992	23.3	4.3
	2.5985	8.4	2.4
	5.1970	5.0	0.9
Santomerse D	0.2923	594.8	92.6
	0.5846	99.6	24.0
	1.1691	15.9	2.3
	2.3382	5.0	0.6
	4.6764	2.7	0.7
	9.3529	2.0	0.9
Trimethyldodecyl-ammonium chloride	1.0663	1233	275
	2.1326	926	128
	3.0466	849	122
	4.3202	518	134

[a] Each standard deviation was based on eight measurements of the wetting time.

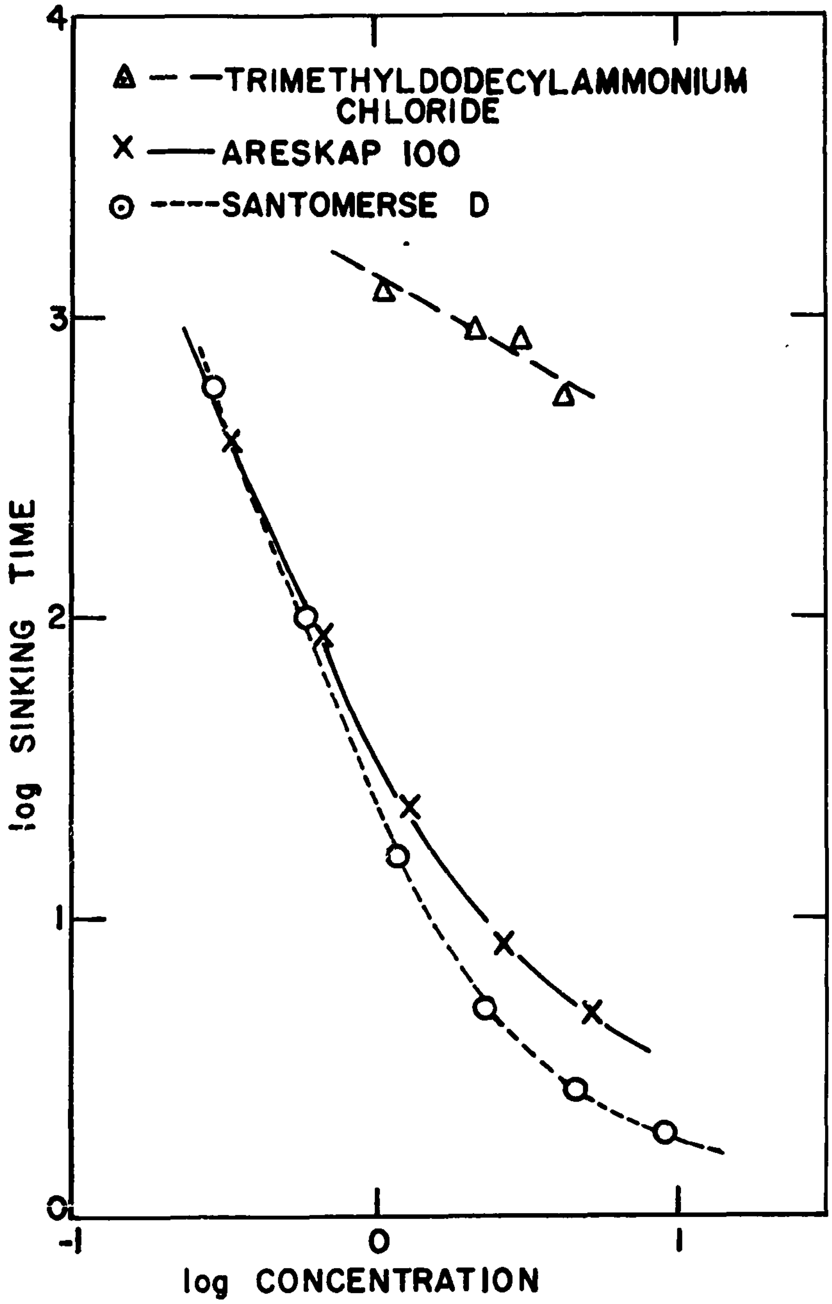


Figure 16. Dependence of wetting time on concentration of solution

(Concentration in g./l.; time in sec.)

DISCUSSION

Dynamic Surface Tensions

Trimethyldodecylammonium chloride

Solutions of trimethyldodecylammonium chloride showed very little or no change in surface tension over the period of time measured. This is very different from the results obtained when solutions of Areskap and Santomerse D were used. The observed surface tensions were lower than that for pure water but much above the equilibrium values.

Because the changes in surface tension were so small, the data would not make a very sensitive test of the rate laws and no tests were performed.

An observation may help to explain the low initial values for surface tension. Before each test the entire glass reservoir and supply system in the apparatus was cleaned with hot chromic acid cleaning solution. This process was continued until the cleaning solution drained in sheets from the surface and did not "break" across the surface. Glassware treated in this way tested clean with distilled water as well as with the cleaning solution. However, as soon as trimethyldodecylammonium chloride solution was placed in the glassware, the liquid film broke and did not drain in a sheet. In other words the surface appeared to be greasy.

Trimethyldodecylammonium chloride is a cationic agent; that is, it is the cation which is adsorbed on the surface. Ordinarily a surface active agent would orient itself to place the hydrophilic part in the water and tend to remove the hydrophobic part from the solution. However, as the cationic surface active ions are adsorbed on glass, the orientation is apparently such that the charged end of the ion is towards the glass. This preferred orientation can be explained in either of two ways.

Glass is made up of a network of silicate ions. At the surface of glass where there is a break in the silicon-oxygen network, oxygen atoms are exposed with unsatisfied valences, making the surface slightly acidic. The surface oxygen atoms would tend to attract either hydrogen from water or any positive ion. Adsorption on glass of positive dye ions was reported by Eitel (23b).

On the other hand, it is possible that there is cation exchange between sodium ions on the surface of the glass and the cations from the surface active agent. The base exchange properties of clays are well known and it is reasonable to expect corresponding behavior from the silicates in glass.

In either case the hydrophilic part of the ion would be oriented toward the glass, leaving the hydrophobic end of the ion exposed to the solution. The aqueous solution is not attracted to the hydrophobic covering on the glass and thus does not wet it.

As the solution flows through tubing coated in this way, a second layer of molecules orient at the surface, and the orientation in this case is with the hydrophobic end out and the hydrophilic in. This layer is not held by the glass surface nor by the previously adsorbed agent on the glass but it travels along with the stream. As a result diffusion to the surface, orientation in the surface, and decrease in surface tension can take place before the stream issues from the orifice. In effect the surface has aged to some unknown extent before it reaches the orifice. This would account in part for the low initial values for surface tension.

Furthermore, slip between the solution and the glass and metal tubes would result in a finite surface velocity at zero age instead of zero velocity as assumed. A finite surface velocity would give rise to wave lengths which are longer than expected and as a consequence the surface tension would appear to be less than it actually is.

Areskap 100 and Santomerse D

Two widely accepted rate laws

$$\frac{\gamma - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-\alpha t} \quad \text{and}$$

$$\frac{\gamma - \gamma_\infty}{\gamma_0 - \gamma_\infty} = e^{-\alpha \sqrt{t}}$$

have been discussed by earlier authors (13-15, 21, 22, 56, 57). The data for Areskap 100 and Santomerse D were used to test these laws in the following forms.

$$\log(\gamma - \gamma_\infty) - \log(\gamma_0 - \gamma_\infty) = -\frac{\alpha}{2.3}t$$

$$\log(\gamma - \gamma_\infty) - \log(\gamma_0 - \gamma_\infty) = -\frac{\alpha}{2.3}\sqrt{t}$$

The results using the first equation are given in Figures 17 and 18. It is seen that for solutions of both surface active agents the points for the two lower concentrations fall very nearly on straight lines but at higher concentrations there is considerable curvature in the lines through the points.

Figures 19 and 20 show the test of the second law. All the points in these graphs fall on or near the appropriate straight lines. At the higher concentrations in most cases the first and last point or two do not lie on the line. This is not surprising as the first points measured on the pure liquids were often slightly in error and it is to be expected

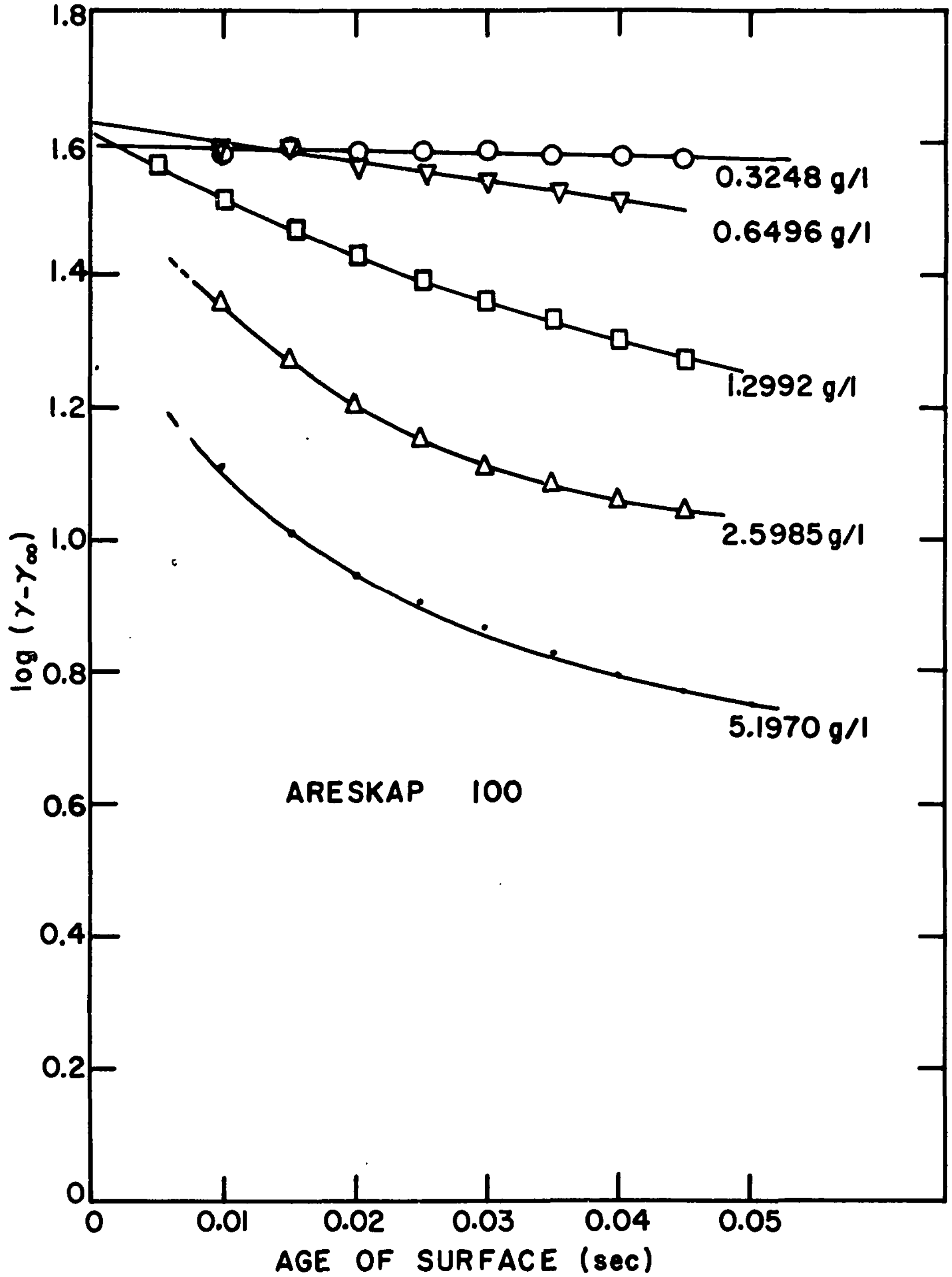


Figure 17. Variation of surface tension with time: Areskap 100

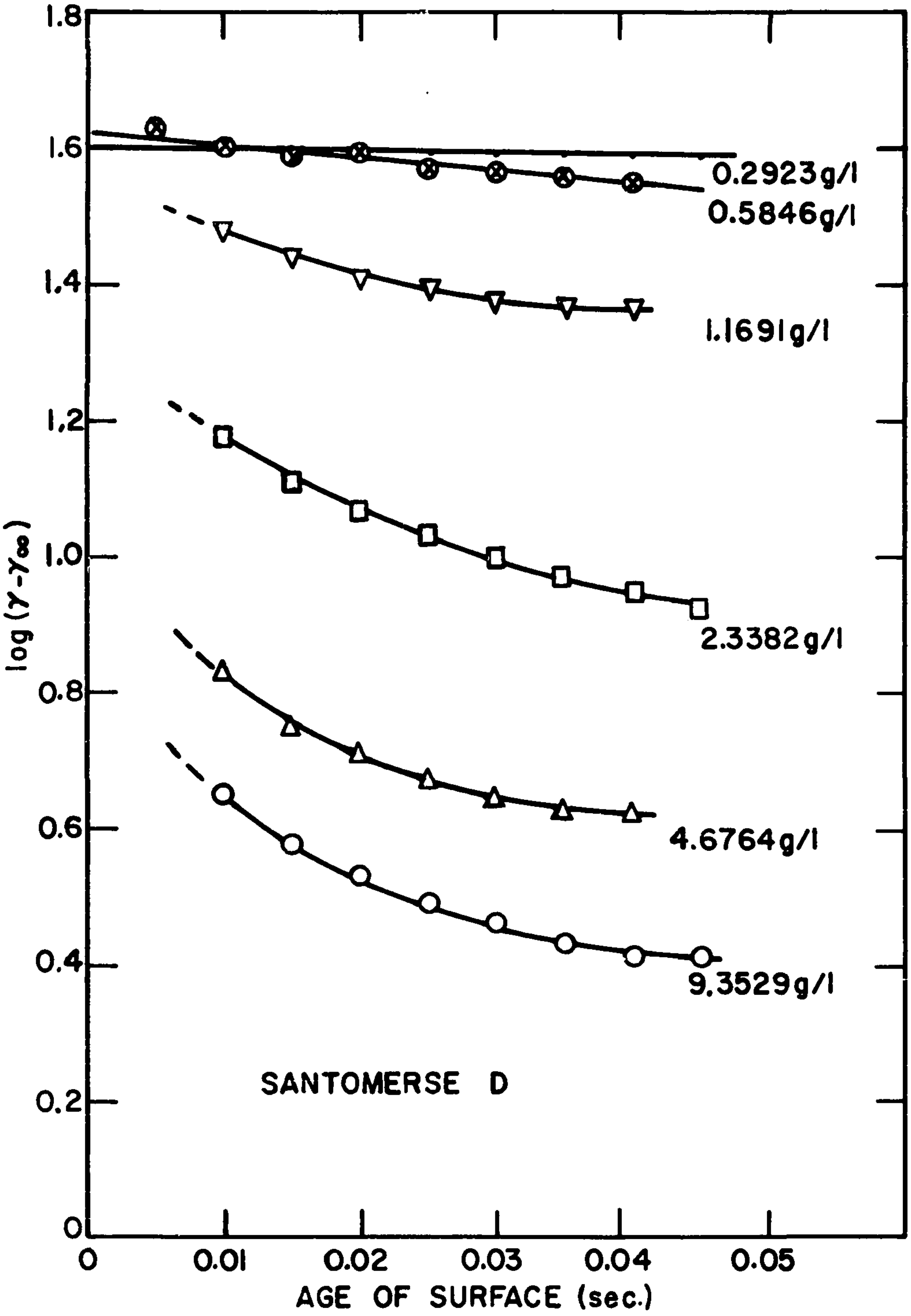


Figure 18. Variation of surface tension with time: Santomerse D

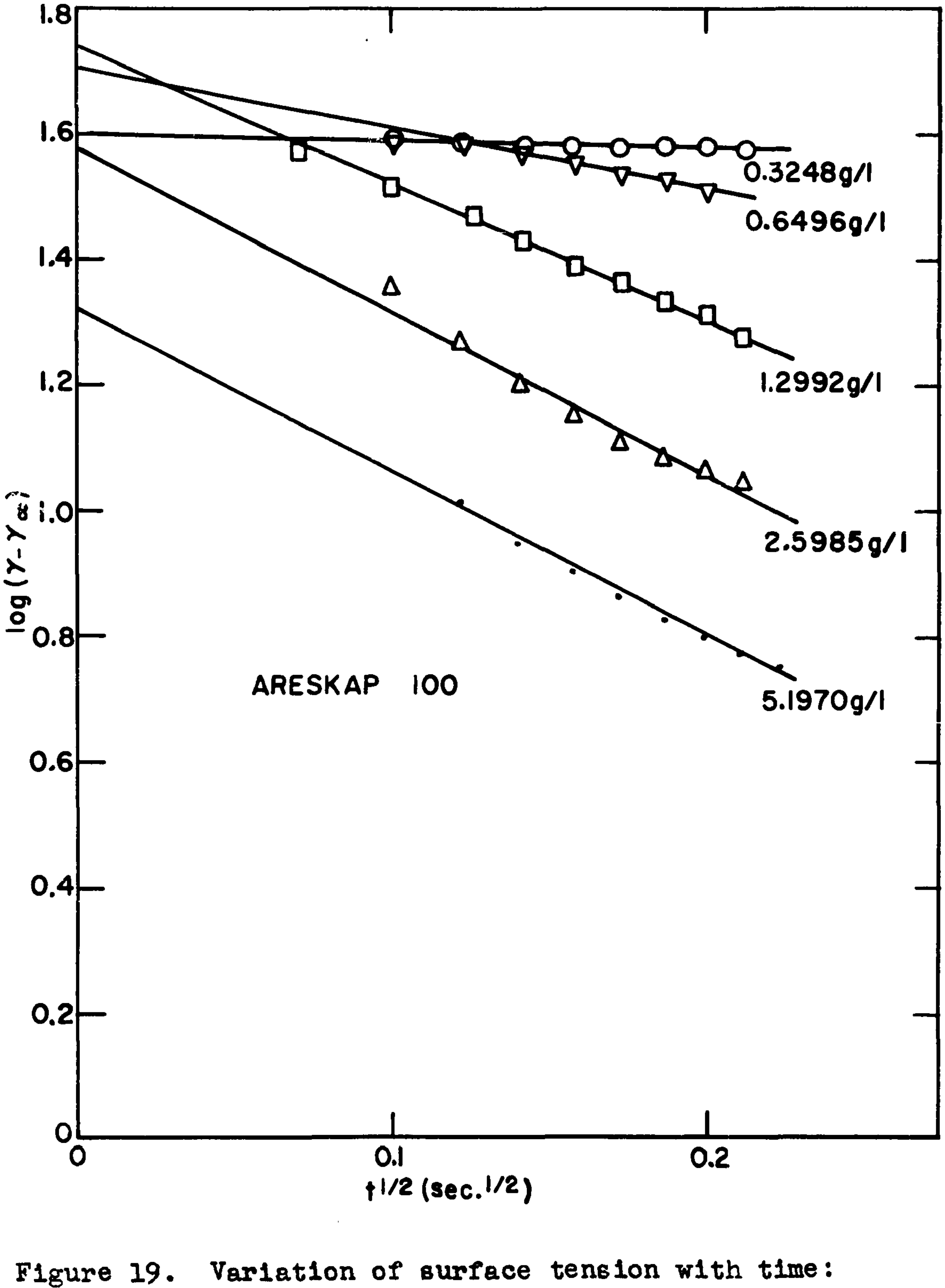


Figure 19. Variation of surface tension with time: Areskap 100

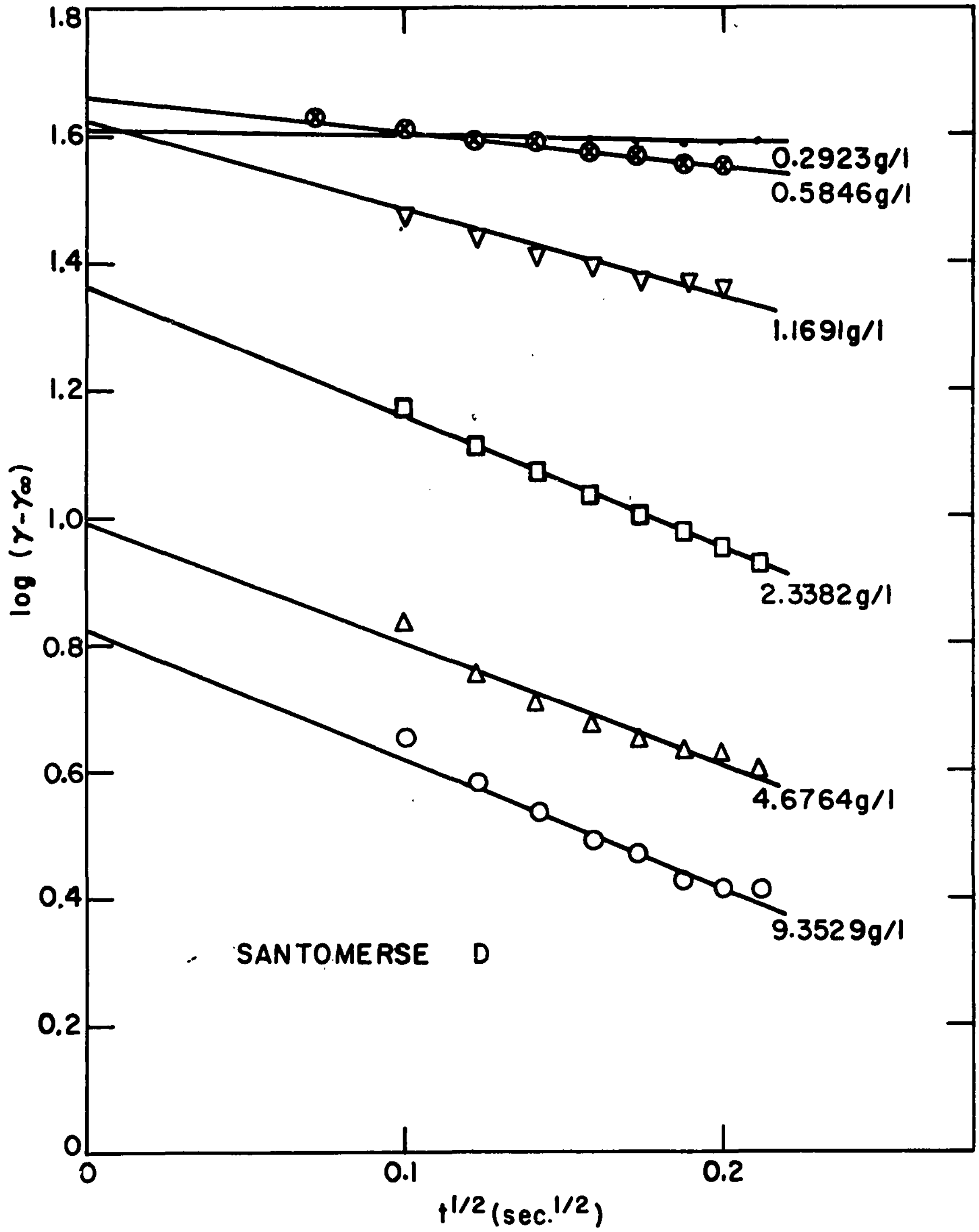


Figure 20. Variation of surface tension with time: Santomerse D

that similar errors in measurement would occur when the solutions were tested. Furthermore, any error in γ would cause a larger percent error in the term $\gamma - \gamma_\infty$ when higher concentrations, and thus lower surface tensions, are involved. Therefore small errors in the first measurements of the surface tension would be more apparent on the more concentrated solutions. Although the errors in γ at the higher ages would be expected to be small, the $\gamma - \gamma_\infty$ error would be much greater on a percentage basis, and this error would be more apparent as γ approached γ_∞ in value, that is, as the age of the surface increased.

It has been suggested by other authors that in a dilute solution the instant a new surface is formed it is so bare of solute molecules that the surface tension is essentially that of water. If this is the case, the term γ_0 would be 72.0 dynes/cm. for work done at 25°C, and for all solutions having the same equilibrium surface tension, $\gamma_0 - \gamma_\infty$ would be the same. If this is true, all the lines for solutions having the same γ_∞ should meet in a point at the ordinate. For Areskap all the solutions tested except the most dilute showed approximately the same γ_∞. Furthermore for Santomerse D the higher solutions all had the same γ_∞. However, the lines for these solutions not only do not meet but for the higher concentrations they are parallel or nearly so.

Although the plot of log ($\gamma - \gamma_\infty$) vs. $\sqrt{t}$ is a straight line, it cannot be said that these data fit the second of the two laws given. For the data to fit, not only should the points fall on straight lines but the intercept of all the lines must be such that γ_0 is 72 dynes/cm. It is very apparent that this last condition is not met.

Although several authors (13, 22, 42, 54, 57) have suggested that adsorption from solution, and thus lowering of surface tension, is diffusion controlled, no one has presented a theory which is fitted by experimental data. The lack of agreement in the past has resulted from incorrect values for the surface tension and age of the surface and from inadequate theories.

In the present work the difficulties which caused others to obtain incorrect dynamic surface tensions have been remedied. Thus it should now be possible to develop a theory which will satisfactorily account for the lowering of the surface tension.

From the present work it is seen that log ($\gamma - \gamma_\infty$), or log ($\gamma_0 - \gamma$), depends on $\sqrt{t}$. It is further observed that for concentrations less than about three grams/liter, the effect of doubling the concentration is to increase the slope of the plot of log ($\gamma - \gamma_\infty$) vs. $\sqrt{t}$ by a factor of about four. In other words below the critical micelle concentration the slope depends approximately on the square of the concentration. Above that point there must be some representation showing dependence of the rate of change of surface tension on the concentration in excess of that required for formation of micelles.

In diffusion-controlled adsorption, Sutherland (54) has shown that, if the adsorption isotherm is of Henry's Law form and the surface is in instantaneous equilibrium with the subsurface, then

$$c\ (0,t) = c\left[1 - e^{x^2}\ \mathrm{erfc}\ x\right]$$

where c (0,t) is the concentration in the subsurface at any time,

$$\mathrm{erfc}\ x = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-y^2} dy \qquad \text{and} \qquad x = \sqrt{Dt}/M\ .$$

M is the Henry's Law constant, such that $\Gamma = Mc$ at equilibrium and at any time $\Gamma(t) = Mc(0,t)$. Γ is the surface excess and D is the diffusion constant.

In effect this treatment can be approached by considering an adsorption isotherm in which the concentration is that of the subsurface and is time dependent. The instant the new surface is formed, solute molecules pass into the surface, leaving the subsurface depleted of solute. As the surface ages, solute particles diffuse from the bulk into the subsurface, the process continuing until the concentrations of the subsurface and the bulk solution are the same. In this representation M is the slope of the adsorption isotherm.

Now if M is not constant (and it is not in this representation), the diffusion problem is non-linear, and no one has been able to solve the diffusion-adsorption problem for any non-linear boundary condition.

A treatment correct in order of magnitude should be expected to result if the mean slope of the adsorption isotherm between c equal to zero and c equal to the equilibrium subsurface concentration is used. If then the detergent adsorption satisfies Langmuir's equation, for concentrations below the critical micelle concentration ($c < c_0$) one would have

$$\Gamma = \Gamma_m \frac{ac}{1 + ac}$$

where Γ_m is the surface excess required for a monomolecular layer. The chord between the points (0,0) and (Γ,c) would have the slope $(a\Gamma_m)/(1 + ac)$ and this would also be the mean slope over the range.

The Langmuir relation is an oversimplified representation of detergent adsorption due to interaction and orientation effects, but it is much less oversimplified than a Henry's Law relation.

At equilibrium, if detergent adsorption follows the Langmuir equation, then

$$\gamma_0 - \gamma_\infty = \Gamma_m RT \ln (1 + ao)$$

and if surface and subsurface are in instantaneous equilibrium we expect

$$\gamma_0 - \gamma = \Gamma_m RT \ln \left[1 + ac(0,t)\right]$$
$$= \Gamma_m RT \ln \left[1 + acG(x)\right]$$

where $G(x) = 1 - e^{x^2} \operatorname{erfc} x$ and $x = \sqrt{Dt}/M$. If we take M, the mean slope, equal to $(a\Gamma_m)/(1 + ac)$, then

$$x = \frac{1 + ac}{a\Gamma_m} \sqrt{Dt}.$$

Hence

$$10^{\frac{\gamma_0 - \gamma}{A}} - 1 = ac\, G(x)$$

where $A = 2.303\, \Gamma_m RT$. For small values of x, $G(x) \approx 1.13x = 1.13 \frac{1 + ac}{a\Gamma_m} \sqrt{Dt}$. Therefore, for small t,

$$10^{\frac{\gamma_0 - \gamma}{A}} - 1 = 1.13 \frac{c\,(1 + ao)}{\Gamma_m} \sqrt{Dt}.$$

In other words the left hand side of the equation should vary as $\sqrt{t}$ for fixed c and small t with a slope, if $ac \gg 1$, which is proportional to c^2. Substantially this is the behavior shown by data from this study.

A better fit of the data can be obtained if M is taken as the average slope over the part of the isotherm which corresponds to the period of observation. The slope of such a line is represented by

$$\frac{a\Gamma_m}{1 + ac(0,\tau)}, \quad \text{where} \quad ac(o,\tau) = 10^{\frac{\gamma_0 - \gamma_\tau}{A}} - 1.$$

(τ = 0.04 seconds) Thus

$$\gamma_0 - \gamma = \frac{10^{\frac{\gamma_0 - \gamma_\tau}{A}} \sqrt{Dt}}{a\Gamma_m}$$

For concentrations above the critical micelle concentration ($c > c_0$), the micelles serve as a source of material in the solution. The micelles are colloidal particles which do not diffuse but which dissolve to maintain the concentration of single particles at c_0. The problem of diffusion from a detergent solution above the critical micelle concentration into pure solvent, both the solvent and solution being taken as infinite in extent, is mathematically equivalent to the problem of heat conduction when a semi-infinite solid below its melting point is placed in contact with a semi-infinite liquid above the melting point. Although a solution has been given for the heat conduction problem (19b), no source problem involving adsorption at a surface has been solved.

Because only single species adsorbed on the surface affect surface tension, for concentrations above the critical micelle concentration (c_0),

$$\gamma_0 - \gamma_\infty = \Gamma_m RT \ln (1 + ac_0).$$

In an attempt to maintain c_0, micelles in the subsurface will dissociate immediately after a new surface is formed. Because the micelles do not diffuse, the subsurface never regains any micelles. It is assumed, as before, that

$$10^{\frac{\gamma_0 - \gamma}{A}} - 1 = ac(0,t),$$

but for solutions above the critical micelle concentration, c(0,t) will depend not only on the diffusion constant (D), the age of the surface (t), and the shape of the isotherm (M), but also on the critical micelle concentration and the extent to which it is exceeded. The dependence can be expressed as

$$c(0,t) = c_0 F(D, t, M, c - c_0), \text{ for } c > c_0.$$

The function F must be of the form that

$$F \rightarrow 0 \text{ as } t \rightarrow 0$$

$$F \rightarrow 1 \text{ as } t \rightarrow \infty$$

$$F \rightarrow G\left(\frac{\sqrt{Dt}}{M}\right) \text{ as } c - c_o \rightarrow 0$$

From a comparison of the present problem with the melting problem previously cited, a form of F which satisfies the conditions is

$$F = G\left(\frac{\sqrt{Dt}}{M} + k(c - c_o)\sqrt{t}\right)$$

where M is now

$$\frac{a\Gamma_m}{1 + ac_o(0,\tau)}.$$

Other forms of F are possible but were not tested as this one gave satisfactory results.

Data from this work were used to test the adequacy of the theory presented. The steps involved are as follows:

1. Determine a value of A. If the molecular dimensions are known, A can be obtained by calculation

   $$(A = 2.303\,\Gamma_m RT = \frac{2.303RT}{\alpha},$$

   where α is the molecular area). Alternately the value of A is obtained by trial and error to be such that

$$10^{\frac{\gamma_o - \gamma}{A}} - 1$$

varies linearly with $t^{\frac{1}{2}}$ for very small values of t. The latter method was used in this work to obtain a value of 30 for A for both Areskap and Santomerse D.

2. Determine the value of a. At equilibrium

$$10^{\frac{\gamma_0 - \gamma}{A}} - 1 = ac \quad \text{for } c < c_0 \text{ or}$$

$$10^{\frac{\gamma_0 - \gamma}{A}} - 1 = ac_0 \quad \text{for } c > c_0.$$

The value of a was established from experimental $\gamma(c_0)$ to be 6.84 liters/gram for Areskap and 6.33 for Santomerse D.

3. Evaluate G(x). For $c < c_0$,

$$G(x) = \frac{10^{\frac{\gamma_0 - \gamma}{A}} - 1}{ac} .$$

For $c > c_0$,

$$G(x) = \frac{10^{\frac{\gamma_0 - \gamma}{A}} - 1}{ac_0} .$$

4. Evaluate x from G(x). $G(x) = 1 - e^{x^2} \operatorname{erfc} x.$

5. Calculate $D^{\frac{1}{2}}$ as

$$\mathcal{D}^{\frac{1}{2}} = \frac{x}{t^{\frac{1}{2}}\, 10^{\frac{\gamma_0 - \gamma_\tau}{A}}} \; .$$

6. Calculate $D = \mathcal{D}\,(\Gamma_m a)^2$. $\Gamma_m a$ is calculated from its equivalent $\frac{A}{2.3RT} \cdot a \cdot 1000$ cm.^{3}/l. $\cdot$ molecular weight. The value of $\Gamma_m a$ for Areskap is 1.171×10^{-3} cm. and for Santomerse D it is 1.06×10^{-3} cm. The values of D in cm.^{2}/sec. are

Areskap

0.65 g./l.	1.22×10^{-7}
1.30 g./l.	2.81×10^{-7}
2.6 g./l.	1.33×10^{-7}
5.2 g./l.	2.22×10^{-7}
av.	1.90×10^{-7}

Santomerse D

0.58 g./l.	3.58×10^{-7}
1.17 g./l.	5.75×10^{-7}
2.34 g./l.	3.84×10^{-7}
4.68 g./l.	4.77×10^{-7}
9.35 g./l.	8.36×10^{-7}
av.	5.26×10^{-7}

7. For solutions above the critical micelle concentration a factor k must be determined which shows the effectiveness of the micelles in decreasing the surface tension

$$x = \left[10^{\frac{\gamma_0 - \gamma_{.04}}{A}} D^{\frac{1}{2}} + k(c - c_0)\right] t^{\frac{1}{2}} .$$

The value of k was determined from an average value for $x/t^{\frac{1}{2}}$ for measurements at each concentration. For the two solutions of Santomerse D above the critical micelle concentration the values of k obtained are 1.07 and 1.01. Only one solution of Areskap was above the critical micelle concentration; for it k is 0.77.

The adequacy of the theory can be tested in two ways. If the slope of the isotherm is closely approximated by

$$10^{\frac{\gamma_0 - \gamma_t}{A}} ,$$

then D should be a constant for all times t and for all concentrations of an agent. Values of D were reasonably constant within each concentration of Santomerse D tested. For low concentrations the value of D increased with t but for the concentrations above c_0 there was a slight decrease in D with t.

Values of D for Areskap showed somewhat more variation than the corresponding data for Santomerse D. Apparently

$$10^{\frac{\gamma_0 - \gamma_\tau}{A}}$$

is a poorer estimate of the slope of the isotherm for Areskap than for Santomerse D. For all concentrations tested the value of D increased with time, although the percent change decreased as the concentration increased. The variation in the average D from one concentration to another did not show any trend.

The second measure of the adequacy of the theory comes from a comparison of D, the diffusion coefficient, obtained by these calculations with accepted values. No values for the diffusion coefficient for the compounds tested could be found in the literature. However, in general, the diffusion coefficients range from 10^{-6} to 10^{-5} cm.^{2}/sec. By this standard the calculated values are somewhat low but are certainly of the proper order.

Consideration of the two tests indicates that the data fit the theoretical presentation and that the adsorption is diffusion controlled. Use of the mean slope for the adsorption isotherm, rather than the isotherm itself, in evaluating M yields values for M which are too low at small ages and too high for longer times. A better estimate of M, which follows the isotherm more closely than the mean slope, would no doubt give more constant values of D with t for each concentration.

The agreement between the theoretical lines based on the calculated diffusion constants and the experimental data is shown in Figures 21 and 22. The agreement between the lines and the experimental data for Santomerse is very good. For the Areskap data the theoretical lines have a lower slope than is indicated by the experimental points.

Equilibrium Surface Tensions

Measurement of the surface tension of the more concentrated solutions of Areskap and Santomerse D gave practically constant values over a period of time. However, for the more dilute solutions considerable time was needed to reach equilibrium. For example, the surface tension of the three highest concentrations of both Areskap and Santomerse D was constant with time and measurements showed good agreement with each other. For the lower concentrations the first values obtained were measurably different from the equilibrium value. Measurements were made over several days to be sure that true equilibrium had been reached.

A further difficulty appeared in measuring equilibrium tensions of the trimethyldodecylammonium chloride solutions. The value obtained was dependent on the rate at which the ring

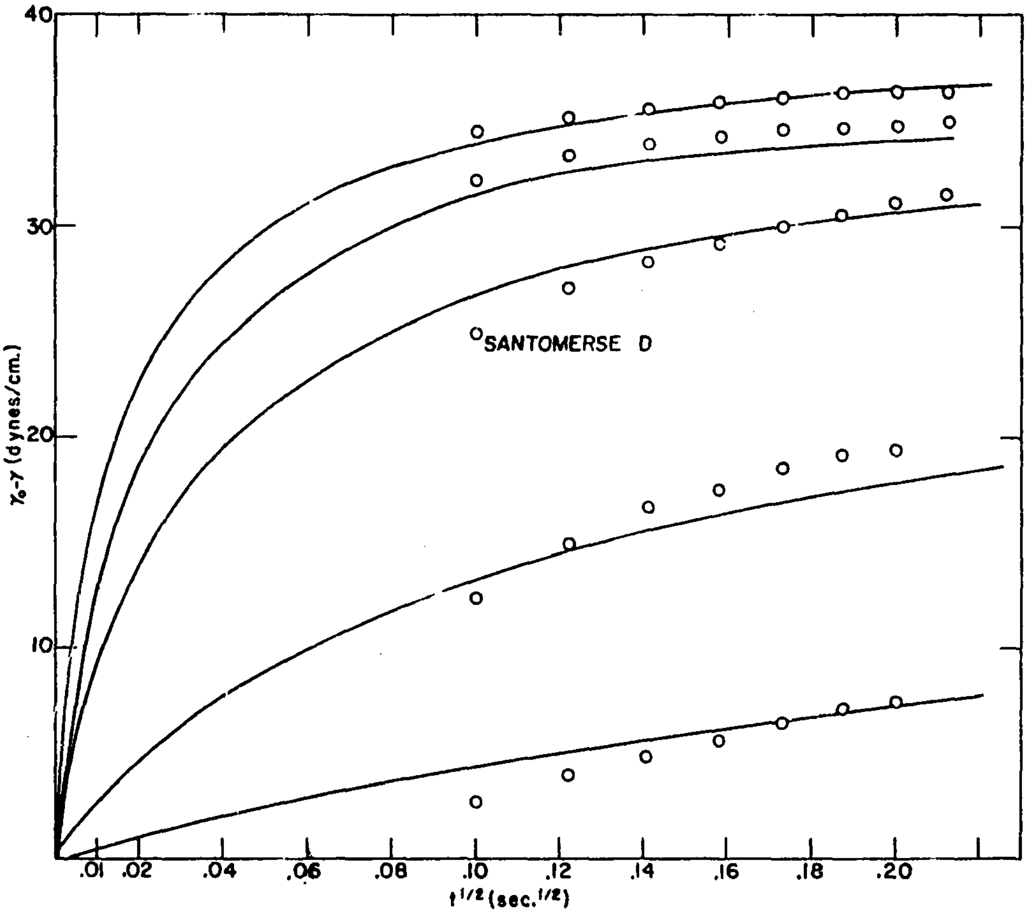


Figure 21. Comparison of theoretical lines and experimental points for the surface tension of Santomerse D

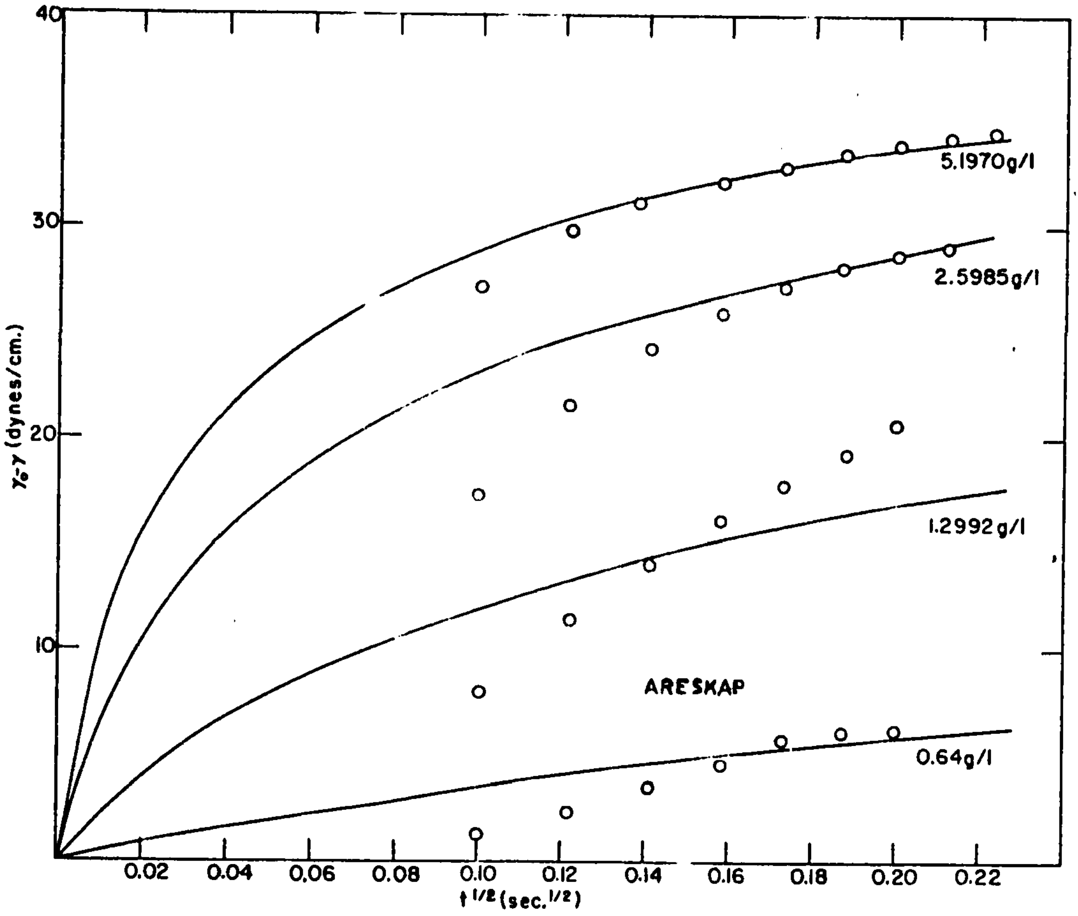


Figure 22. Comparison of theoretical lines and experimental points for the surface tension of Areskap 100

was raised. If the ring was lifted quickly, the values obtained were higher than if the ring was raised more slowly or if the ring was raised part way and allowed to stand in that position for a time before the ring was finally pulled away.

As the ring is raised, new surface is formed, and the new surface is initially low in surface active agent. If solute ions diffuse to the surface rapidly, formation of new surface would not cause the observed surface tension to be appreciably higher than the true equilibrium value; however, for other solutes true equilibrium values might not be obtained in this way unless the ring were raised extremely slowly.

Because of this difficulty the values obtained for the equilibrium surface tension for trimethyldodecylammonium chloride may be biased by a small amount. However, formation of the new surface in measuring equilibrium surface tensions of solutions of the other surface active agents did not cause noticeable increase in surface tension.

One measure of the purity of a surface active agent is the effect of dilution on the equilibrium surface tension. If a single surface active material is present, no minimum is observed in the surface tension-concentration curve, but if a more strongly adsorbed agent is present as an impurity, it also will be adsorbed and will lower the surface tension below that for the pure compound.

It is probable that neither the Santomerse D nor the Areskap was a single agent. Neither material could be purified by recrystallization. In the manufacture of Santomerse D several isomers are formed. Furthermore, long chain alcohols are likely to be present as a result of side reactions. The extent of impurity in the Areskap was evidently small, as the minimum surface tension was less than one dyne/cm. below that for more concentrated solutions. There was apparently more impurity in the Santomerse D as the minimum in this case was four dynes/cm. below the surface tension of the more concentrated solutions.

Sinking Time Tests

Fabric sinks in a liquid when the liquid advances into the capillary spaces to a great enough distance to increase the bulk density of the fabric above that of the liquid. If d is the average distance to which the liquid must penetrate the capillary before sinking occurs, then

$$t_s = \frac{d}{v} \qquad (1)$$

where t_s is the sinking time and v is the average velocity of the liquid travelling into the capillaries.

For uniform motion of the liquid front, the net force acting on the front must be zero. This is true when the surface forces acting to move the liquid are just equal to the viscous drag, which in turn is proportional to the velocity of the moving front. The surface force is given by $\gamma_S - \gamma_{SL} - \gamma_L \cos\theta$ where γ_S is the surface tension of the fibers in the fabric, γ_{SL} is the fiber-liquid interfacial tension, γ_L is the surface tension of the liquid, and θ is the contact angle.

The above expression can be rewritten in terms of the pure solvent and changes in surface tension from that of the pure solvent.

$$\gamma_S - \gamma_{SL} - \gamma_L \cos = \gamma_S^o - (\gamma_{SL}^o - \Delta\gamma_{SL}(t)) - (\gamma_L^o \cos\theta - \Delta\gamma_L(t)\cos\theta)$$

$$= \Delta\gamma^o + \Delta\gamma_{SL}(t) + \Delta\gamma_L(t)\cos\theta \qquad (2)$$

The three terms involving the pure substances are collected in $\Delta\gamma^o$. $\Delta\gamma_{SL}$ and $\Delta\gamma_L$ are the decreases in interfacial and surface tensions which result in time t from addition of surface active agent to the solvent. In summary

$$v = K(\text{viscous drag}) = K(\text{surface forces})$$

$$= K(\Delta\gamma^o + \Delta\gamma_{SL}(t) + \Delta\gamma_L(t)\cos\theta) \qquad (3)$$

From the work of Bartell and others (8a, 39) it is assumed that the changes in surface and interfacial tensions are proportional to each other. If $\Delta \gamma_L(t) = b \Delta \gamma_{SL}(t)$, then $\Delta \gamma_L(t) \cos \theta + \Delta \gamma_{SL}(t) = (b + \cos \theta) \Delta \gamma_L(t) = \beta \Delta \gamma_L(t)$. Thus

$$v = K \left[\Delta \gamma^o + \beta \Delta \gamma_L(t) \right] \tag{4}$$

The peripheral velocity given by equation (3)' depends on t, that is, on the surface age; if this were assumed to increase uniformly, starting from the instant of cloth-solution contact, the rate of penetration should likewise increase uniformly. Since the sinking times involved are all in excess of two seconds and since the surface tension depression rate for most solutions studied was such as to bring the surface tension values nearly to equilibrium in times short compared to this, the rate of penetration would depend principally on the equilibrium surface tension. However, solutions of nearly the same equilibrium surface tensions show marked variations in their rate of cloth penetration, contrary to the uniform aging hypothesis. The solutions behave, in the penetration experiments, as if their surfaces had aged for periods short compared to the sinking time. This behavior suggests that the penetration, while perhaps uniform from a macroscopic view, is intermittent on a microscopic scale. A plausible mechanism for such an intermittent penetration can be advanced and leads immediately to a quantitative theory of the sinking of cloth by solution penetration.

Bartell and Shepard (8b) have shown that an apparent contact angle formed on a rough paraffin surface will exceed the true contact angle by approximately the angle between the asperity face and the mean plane of the surface. This result appears very reasonable, since the volume of liquid required to maintain the true contact angle on the side of the asperity away from the liquid source will be so great that the liquid will spread up the side of the next asperity immediately after it has reached the bottom of the first. This process is illustrated in Figure 23. The spreading of the liquid will hence be intermittent; that is, it will move slowly down the far faces of asperities and rapidly up the near ones.

The proposed mechanism requires that the solutions make non-zero contact angles with the fibers and that there be roughness on the surface of the yarns. Fowkes (26) has shown that both water and detergent solutions form non-zero contact angles on cotton fibers. Roughness in cotton fabrics can be expected both from the roughness of the fibers themselves and also from the fact that the yarns consist of log-pile-like bundles of fibers.

For simplicity the asperities can be considered to have equal plane faces. If y is the length of one face, then the

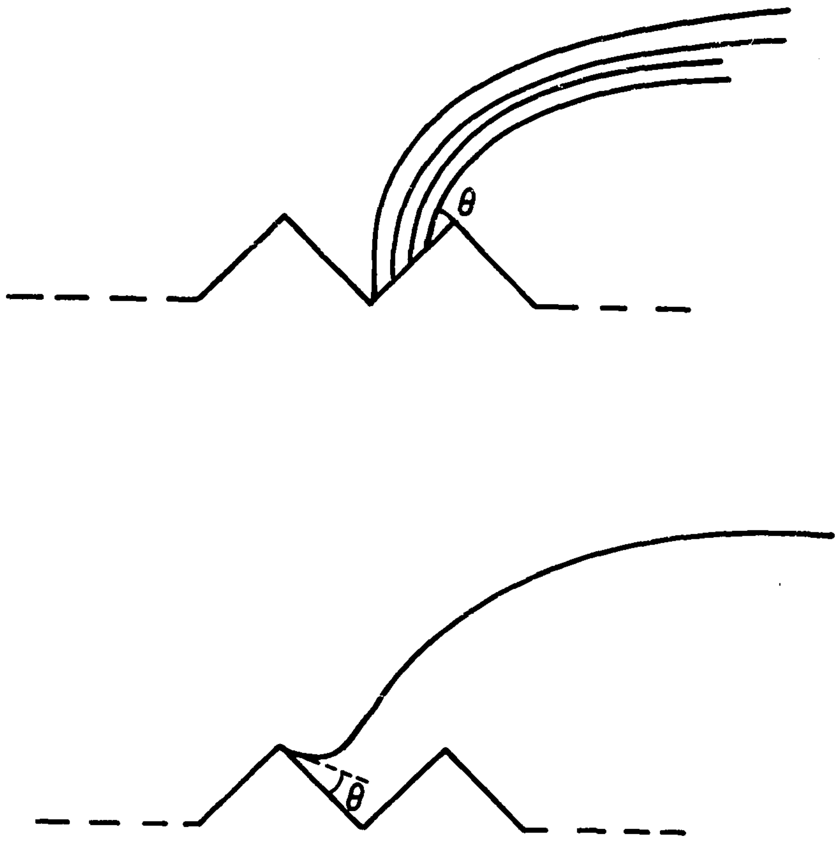


Figure 23. Schematic diagram of liquid passing over an irregular surface

time τ required for the liquid to advance down the far side of an asperity must satisfy the following equation

$$y = \int_0^{\tau} v \, dt = K \int_0^{\tau} \left[\Delta\gamma^\circ + \beta \Delta\gamma_L(t) \right] dt \qquad (5)$$

Since τ is small, and thus $\Delta\gamma_L$ is small,

$$10^{\frac{\gamma_0 - \gamma}{A}} - 1 = e^{\frac{2.3(\gamma_0 - \gamma)}{A}} - 1 \approx \frac{2.3(\gamma_0 - \gamma)}{A} = acG(x) \qquad (6)$$

Since x is also small

$$G(x) \approx 1.13\, x = \mathcal{D}^{\frac{1}{2}} Q t^{\frac{1}{2}} \qquad (7)$$

where

$$Q = 10^{\frac{\gamma_0 - \gamma_{.04}}{A}}$$

below the critical micelle concentration and

$$10^{\frac{\gamma_0 - \gamma_{.04}}{A}} + \frac{k}{\mathcal{D}^{\frac{1}{2}}} (c - c_0)$$

when micelles are present. Hence

$$\Delta\gamma_L(t) \approx \frac{1.13}{2.3} AacQ\mathcal{D}^{\frac{1}{2}} t^{\frac{1}{2}} \qquad (8)$$

and therefore

$$y = K\left[\Delta\gamma^{\circ}\tau + \frac{2(1.13)}{3(2.3)} Aac\beta\, Q\mathcal{D}^{1/2}\right]^{3/2} \qquad (9)$$

If the rate of motion up the near side of the following asperity is very fast, then the periphery travels a distance 2y in time τ, and the mean velocity is

$$\bar{v} = \frac{2y}{\tau} = 2K\left[\Delta\gamma^{\circ} + \frac{2(1.13)}{3(2.3)} Aac\beta\, Q\mathcal{D}^{\frac{1}{2}}\tau^{\frac{1}{2}}\right] \qquad (10)$$

The change in order of magnitude of sinking time caused by addition of surface active agent is such that the first term on the right must be very small compared to the second term. If $\Delta\gamma^{\circ}$ is ignored, equation (5) can be solved for τ and the result substituted in equation (10) to obtain

$$\bar{v} = 2y^{1/3}\left[\frac{2(1.13)\beta ac\ K}{3(2.3)} Q\mathcal{D}^{\frac{1}{2}}\right]^{2/3} \qquad (11)$$

Hence

$$t_s = \frac{d}{\bar{v}} = \frac{d}{2}y^{-1/3}\left[\frac{2(1.13)}{3(2.3)} K\beta\, acQ\mathcal{D}^{\frac{1}{2}}\right]^{-2/3} \qquad (12)$$

or

$$\frac{1}{t_s} = \frac{2y^{1/3}}{d}\left[\frac{2(1.13)}{3(2.3)} K\beta\, acQ\mathcal{D}^{\frac{1}{2}}\right]^{2/3} \qquad (13)$$

For a particular surface active agent and any one fabric the only variables in the last term are the concentration and Q.

If all the constants are combined into one, K', and X is substituted for cQ, equation (13) becomes

$$\frac{1}{t_s} = K'X^{2/3} . \tag{14}$$

Hence a plot of $1/t_s$ against $X^{2/3}$ should be linear. The general correctness of this conclusion is illustrated in Figure 24.

By similar reasoning the sinking time in pure solvent should be

$$t_s^o = \frac{d}{\bar{v}} = \frac{d\,\tau}{2y} = \frac{d}{2y} \cdot \frac{y}{K\ \Delta\gamma^o} = \frac{d}{2K\ \Delta\gamma^o} \tag{15}$$

The success of the theory presented suggests that adsorption at solution-cloth and solution-air interfaces are kinetically similar (since the theory includes the assumption that the boundary tension depressions at these interfaces were proportional at any time). Both processes hence must proceed by similar rate-limiting mechanisms, and from the treatment found to be successful in representing detailed kinetic data for adsorption at the water-air interface it appears that the slow step in both processes is diffusion of surface active agent to the interface.

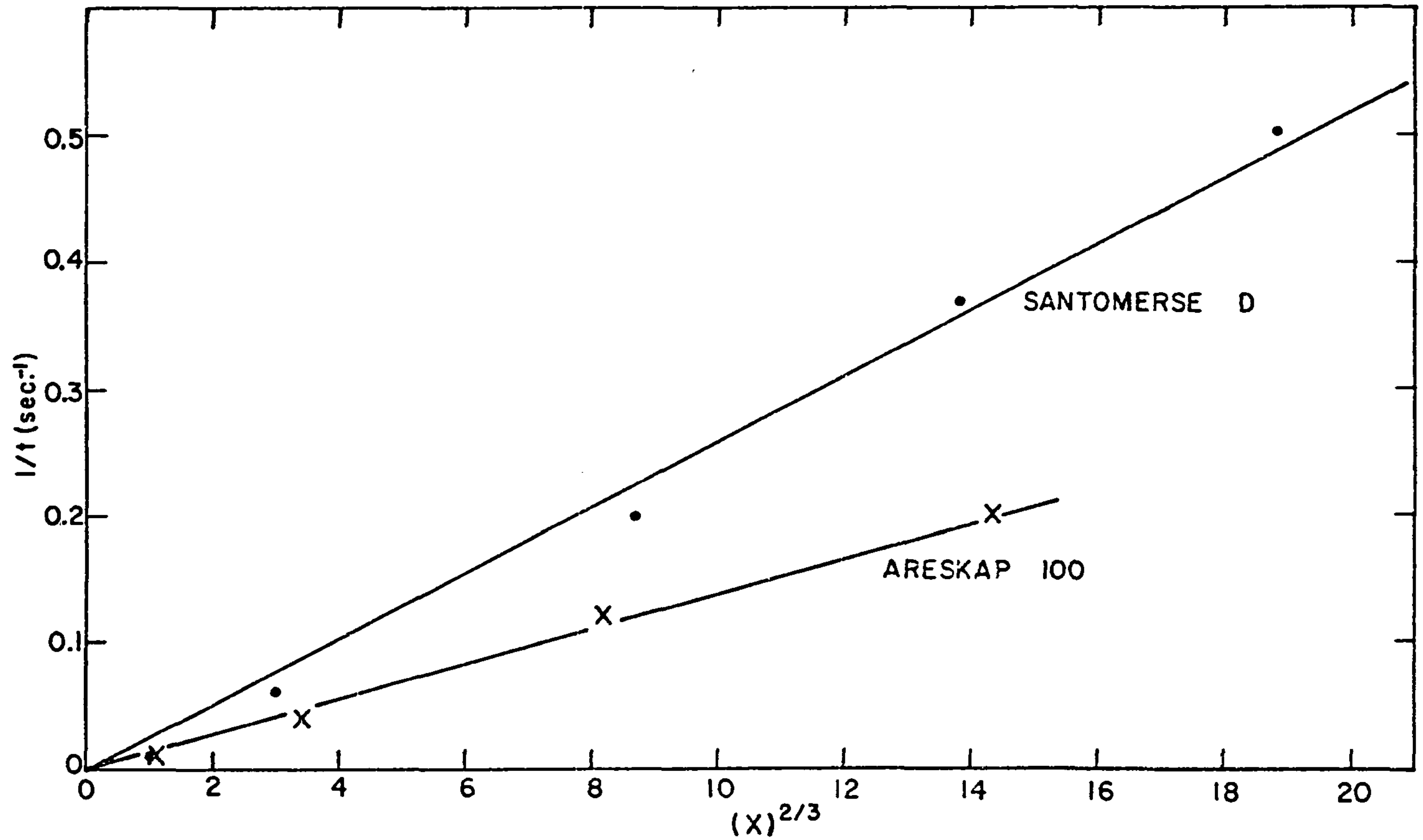


Figure 24. Dependence of sinking time on generalized coordinate X

SUMMARY

1. The principles involved in the determination of dynamic surface tensions by the vibrating jet method have been examined. Previous methods for calculation of surface tensions and surface ages are shown to be inaccurate and fundamentally erroneous. An accurate theory appropriate for these calculations was developed in collaboration with other workers in this laboratory and its validity demonstrated experimentally.
2. The corrected vibrating jet method has been applied to the determination of the dependence of surface tension on surface age and bulk concentration for aqueous solutions of trimethyldodecylammonium chloride, Santomerse D, and Areskap 100. An approximate theory based on the assumption of diffusion-controlled adsorption was developed and shown to furnish a reasonably satisfactory representation of the observed data.
3. Sinking times as determined in the canvas disc wetting test have been measured as functions of concentration for aqueous solutions of these same surface active agents. A theory was presented relating sinking times

to rates of surface tension depression. The success of this theory in representing observed data suggests that the penetration of liquid into cloth is intermittent and that the adsorption of agent at the cloth-solution interface is also diffusion-controlled.

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