STUDIES IN DETERGENCY

by

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INTRODUCTION

Soap solutions are the most efficient, the most eco-
nomical, and the most widely used cleansing agents known.
Water solutions of soaps have relatively low surface ten-
sions, high viscosities, and the power to stabilize sus-
pensions of solids and liquids. When soap is used in the
laundry, alkaline builders are nearly always added since
it is generally believed that these salts increase the
detergent power of the soap. Many workers have made
measurements of the physical and chemical properties of
soap solutions without satisfactorily establishing any of
them as a quantitative measure of detergent power. The
work represented by this paper was attempted in an effort
to establish some relationship between the surface tension,
pH value, and the detergent value of soap solutions when
the detergent value is measured by controlled washing tests.

HISTORY OF SOAP

The cleansing action of soap has been known since Biblical times. Feldhaus-Friedenau (1) states that the ancients were familiar with salt, sodium carbonate, honey, bone meal, bran, Lemnian earth, pumice, and decomposed urine as washing materials. He says that the last named product was used mainly for its ammonia content and was almost universally employed by the old Roman laundries. He states that mural paintings were discovered in 1775 at Civitia, Italy, which show an old Roman laundry in one of the scenes and that a well preserved laundry was unearthed in Pompeii in 1826. He states that Pliny, in 190, reports that the first soap was made by the Gauls from goat tallow and wood ashes and was used by them as a hair pomade. He reports that Galenos, in 200 A.D., gave the first mention of the use of soap as a cleansing material. Soap boiling, according to Feldhaus-Friedenau (1), was first authentically mentioned in Germany about 805 under Charlemange. He states that during the Middle Ages, soap was used mainly by the more wealthy people as a cleansing agent for fine fabrics, and that by the seventeenth century, a patent had been issued in England to a band of soap boilers, which resulted in a very large consumption of soap in that country.

Chevreul (2) as a result of his researches on fats and oils explained the chemical constitution of soaps. He stated that soap was the metal salt of long chain fatty acids which were produced by the hydrolysis of fats. Chevreul (2) also gave the first theory of the detergent action of soap solutions.

THEORIES OF DETERGENCY

The first theory as to the cleansing action of soap solutions was that of Chevreul (2) in 1823. He showed that soap, dissolved in water, hydrolysed into free alkali and acid salts of the fatty acids. He assumed that all dirt was covered with a film of fatty substance and as a result of this film, the particles of dirt adhered to surfaces. The free alkali was thought to saponify this film of fatty material, which released the dirt particle, and allowed its suspension in the suds. He assumed that rinsing would wash away and prevent redeposition of the suspended dirt particles. He also believed that the property of foaming and the emulsifying power was due to the undecomposed soap in the solution. This theory of the detergent action was not disproven for almost a century.

According to Fall (4), with only one or two exceptions, all of the theories of detergent action, up to 1903, were founded on the belief that the alkali of hydrolysis of the soap was the active agent.

Hillyer (3) published an investigation in 1903 which completely disproved the theory that free alkali was responsible for the cleansing action of soap solutions. He showed that the emulsifying power of soap solutions could not be duplicated by concentrated solutions of alkalis and hence, that the emulsifying power of soap solutions could not be attributed to the free alkali produced by the hydrolysis of the soap. He further showed that concentrated solutions of alkali did not have the property of wetting oily material as did soap solutions. Finally, he demonstrated that only solutions with low surface tensions were able to form stable emulsions. He showed that saponin emulsified through the formation of a solid surface film instead of through low surface tension. He concluded that the cleansing action of soap solutions was due to the soap itself and not to any other agents which might be present in the solutions.

In 1909, Spring (5) showed that soap could suspend
and carry oil-free lamp black, alumina, iron oxide, and
silica, through filter paper. He showed that soap made
these particles less adherent to fibers and to each other.
He also proved that part of the dirt is free from the
surrounding film of oil and that this film was not neces-
sary for detergent action. Spring stated that the attrac-
tion of both fabric and dirt for soap exceeds the attraction
of the fabric for dirt and of dirt particles for each other.

Salmon (6) has investigated the conductivity of soap
solutions and has found very high values for specific
conductivity at certain concentrations. It was at first
assumed that this conductivity was due to the carrying of
current by the NaOH formed by hydrolysis. McBain and
Salmon (7) have disproven this explanation by their
measurements of the degree of hydrolysis by means of pH
determinations. With solutions of sodium palmitate, the
ionic hydroxyl concentration was found to be about N/1000
or about 6% hydrolysed. They explain the abnormal increase
of equivalent conductance, observed with the higher fatty
acid salts, by the formation of highly mobile colloidal
anions from the fatty acid salts. To explain this rise in
equivalent conductivity, they make the assumption that the

anion is a complex aggregate of a number of simple anions,
each of which carries its normal charge. These several
charges when distributed over the surface of the colloid
are sufficient to raise the charge to a value that gives the
increased mobility even though the frictional resistance
is increased with the larger particle.

McBain and Salmon (7) used the conductance data in
combination with indirect vapor pressure measurements to
make approximate calculations of the amounts of various
constituents in soap solutions. They were able to show
that the particles in soap solutions and gels were aggre-
gates of the simple soap molecules. If the solution were
very dilute, then the solute was largely a molecular
solution such as a solution of sodium acetate.

The colloidal theory of detergency resulted from this
work on soap solutions. According to this theory, a soap
solution is composed of simple molecular soap solution and
charged soap particles which are aggregates of the simple
units. According to Salmon (6), these soap micelles
migrate toward the anode when under a potential, with a
rate equal to the potassium ion. When these particles come
in contact with dirt particles, which are also charged

particles, they neutralize the charges and adsorb the
dirt particles thus preventing flocculation or deposition.
Fall (4) states that the distinctive characteristic of soap
solutions is the low surface tension imparted to the solu-
tion by the soap and that on this property depends its
great power of (a) wetting surfaces, (b) dispersing and
suspending small solid particles and droplets of liquids
immiscible with water, and (c) lubricating surfaces and
dirt particles.

If the dirt is adsorbed on a solid surface, soap
solutions, because of the low surface or interfacial ten-
sions, are able to wet both the dirt and the surface. They
also lubricate the solids, making for an easy separation,
probably by coating both solids with the viscous soap
solution. Either mechanical agitation or the bombardment
of the dirt particles by the soap micelles loosens the
lubricated dirt particle. After, it is adsorbed by the
particle which prevents redeposition on the solid surface.
Simple rinsing removes both from the solid.

It is certain that any theory which is to be the final
explanation of detergent action must consider the soap
solution; the dirt, whether liquid or solid; and the surface

to be cleansed, each as a colloid. Many other theories of
detergent action have been given at various times, but the
colloidal theory seems to be the accepted theory at the
present time.

The X-ray investigations of Thiessen and
Spychalski (9) showed that soap micelles have the structure
of the crystalline neutral water free fatty acid salt.
Water fills only the intercellular and capillary spaces
in the soap gel. The molecules of the salts are arranged
at right angles to the long axis of the rod like micelles.

METHODS OF DETERMINING DETERGENCY

McBain, Hawthorne, and King (8) developed the first
quantitative method for the determination of detergent
power. This is an application of Spring's method (5) in
which the carbon black carried through a filter paper by the
soap solution is estimated. The carbon black carried
through the paper in a definite volume of solution was
estimated by comparison which allowed quite some error.
The quantity of carbon, and hence the detergent value,
varies with the filter paper, the method and pressure of
folding, and with the amount of carbon retained in the
filter paper itself. It seems that this method would give

very unsatisfactory results because of its variables.

Fall (4) evaluates detergent power of soap solutions by suspending colloid mill manganese dioxide under definite, controlled conditions and then volumetrically determines the amount in suspension. This method eliminates the difficulties of the McBain method (8) and the author claims that quantitative results can be obtained by using the method for determining manganese dioxide in pyrolusite.

The Fall method of determining detergent power was tried several times with out success. It was found impossible to secure check results in solutions of soap with a high proportion of unsaturated fatty acids.

Chapin (10) determines the relative deflocculating or detergent efficiencies by a method based on the behavior of powdered flake graphite in suspension. He states that a white crescent appears in the foam, at the junction of the solution and the foam, when the optimum concentration has been reached.

Stericker (11), White and Marden (29) and others have used measurements of surface tension against air, drop numbers and foam numbers as measures of detergency.

Stericker (11), Millard (12), Hillyer (3), Elledge and Isherwood (13), Briggs and Schmidt (14), Lenher and Buell (15), Richardson (16), and others have used measurements of interfacial tension against oils as detergent values.

Papaconstantinou (17) valued the protective action of soap solutions by measuring the gold numbers.

Stericker (11), Rhodes and Brainard (18), Snell (19), Morgan (20), and others have used direct washing with soiled cloth under controlled conditions of temperature and concentration. In these tests, the dirt was suspended in a solution of fat and oil containing solvent. The cloth was then soiled with the oil covered particles which according to Snell (19) represents the dirt most difficult to remove.

Vincent (21) states that concentrated soap solutions are good detergents because of their extremely efficient wetting and emulsifying ability.

Mullin (22) states that cleansing action increases almost as a straight line function of the pH. Rhodes and Bascom (23) show that maximum detergent effect is obtained at a pH of 10.7. They state that the detergent power of a neutral soap first increases and then decreases

as the alkalinity of the solution is increased. Also the
detergent power seems to increase with the valence of the
anion present.

Mikumo (24) states that washing tests indicate that
detergent action of soaps runs parallel with the surface
tension and interfacial tension against kerosene and is
very high when the surface tension is lowest. This, he
says, indicates that the active detersive agents in pure
soap solutions are highly dispersed components, especially
simple soap molecules, fatty acid ions, or very fine
colloid units.

Van der Werth (25) believes that there are three dom-
inant factors which determine cleansing power; adsorption,
emulsifying power, and wetting ability. He also believes
that washing tests are essential for evaluating detergents.

Many mechanisms of detergent action and many methods
have been devised for the measurement of detersive action,
but none of them have proven to be direct measures of this
power. Washing tests performed with soiled cloth and under
controlled conditions have become the most used methods of
evaluating detergent power.

EXPERIMENTAL METHODS

Surface Tension

Surface tension measurements were made at 60°C. with a Findlay's surface tension apparatus. The densities of the solutions were considered to be the same as water at the same temperature. The equation (27) for relating surface tension in dynes per centimeter to capillary rise is :

$$\gamma = \tfrac{1}{2} h d g r.$$

pH Value

The pH value was measured with a potentiometer. It was found that a platinum electrode would give check results in alkaline soap solutions. The equation (28) for the calculation of the pH value with a standard calomel half cell using saturated potassium chloride solution and a platinum electrode at 25°C. is :

$$pH = \frac{E_T - 0.2464}{0.0591}$$

Detergent Power

The detergent power of the soap solutions was determined by the method outlined by the Detergents Committee Report to the Oil Chemists' Society (26) in 1931.

Figure I
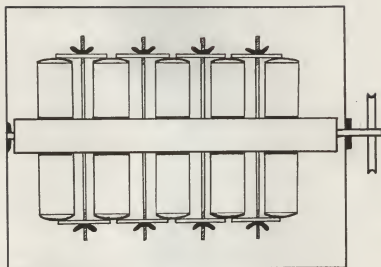
Jars Arranged in Washing Machine.

Figure I represents the washing machine used in the detergent tests. This machine is similar to the Launderometer manufactured by the Atlas Devices Company, Chicago, Illinois and the jars are Atlas E-Z Seal pint jars. The washing machine consists of a horizontal shaft geared to a motor such that it can be rotated at a speed of 40 r.p.m. It is arranged to hold one-pint jars placed

radially about the shaft with the base of the jars two
inches from the center of the shaft. The temperature of
60°C. is maintained by means of water into which the jars
dip during part of each revolution.

"Utica" brand sheeting, manufactured by the Utica
Steam and Mohawk Valley Cotton Mills, Utica, New York,
having 27 threads per inch in the warp and 25 threads per
inch in the filling and free from sizing, was cut into
strips about 13 inches wide. These strips were soiled by
immersing in a water suspension of oil free carbon black
carrying about 20 grams per liter. The carbon black used
was grade "J" supplied by L. Martin Company of Philadelphia.

The strip of cloth was first wet with distilled water,
then placed in the carbon suspension for a short time and
then passed through the rolls of a tightly set clothes
wringer. This operation is repeated until the color
ceases to become deeper, then it is placed in a jar and
shaken with fresh portions of distilled water until the
carbon black no longer appears in the rinse water. The
strip is dried at room temperature, cut into pieces about
3½" x 6" and sewed into bags in which 50 Monel metal balls
1/4 inch in diameter are placed.

The detergent solutions were prepared by dissolving definite quantities of soap or soap and builder in a small volume of distilled water and then diluting to volume at 60° C. The soap and builder concentrations are expressed as per cent by weight.

Two test bags are placed in each jar with 100 cc. of the detergent solution. The jars are capped and clamped into the washing machine. The jars are rotated for twenty minutes at 40 r.p.m. and at 60° C. The solution is then poured from the jars and 100 cc. of fresh solution is added to each jar, and rotated again. After six twenty minute washings, the bags are rinsed with three successive 100 cc. portions of distilled water at 60° C. The bags are then cut open and dried in air on a glass plate.

The detergent power of the solution is determined with the use of an Ives tint photometer. The whiteness of the original soiled unwashed cloth is determined by direct comparison with a magnesia block and stated as per cent whiteness since the Ives scale has 100 divisions. The whiteness of the washed pieces is measured in the same manner and the increase in whiteness in Ives units is taken as a measure of the detergent power of the solution in which the cloth was washed.

It is admitted that this method does not take into consideration the different kinds of dirt, the different kinds of cloth, and other variables. According to Vail (26), soil of this type is the most difficult to remove from fabric and therefore it should be the type for determining detergent power.

Electrodialysis of Sodium Oleate

The soap used in all tests was Merck's "Sodium Oleate, Neutral Powder". In order to determine whether the minute traces of salts in the soap had any effect on the measured properties, a quantity of the sodium oleate was electro-dialyzed against distilled water with a six volt current until the spectroscope showed only the very faintest sodium lines. The liberated fatty acid was dried to constant weight in a vacuum oven at $50°C$. Soap was formed by treating the free acid with its chemical equivalent of sodium hydroxide in water solution. The detergent solutions of definite soap concentrations were made from the electro-dialyzed sodium oleate solution.

EXPERIMENTAL DATA

Table I

Detergent Value, pH, and Surface Tension
of Sodium Oleate Solutions

No. of Samples	Detergent Solution % by wt.	Increased Whiteness Ives %	pH Value	Surface Tension Dynes/cm.
2	0.00 Na oleate	11.6	8.3	67.1
6	0.01 " "	18.9	8.5	36.4
6	0.03 " "	21.1	9.7	27.4
6	0.05 " "	18.8	10.0	25.8
6	0.07 " "	16.3	10.15	25.3
6	0.10 " "	12.4	10.2	25.8
6	0.12 " "	15.0	10.1	24.1
6	0.15 " "	11.9	10.3	25.7
6	0.20 " "	14.1	10.2	24.9

Note: No. of Samples represents total number of cloth pieces washed in each solution.

Table II

Detergent Value, pH, and Surface Tension
Electrodialyzed Sodium Oleate Solutions with Caustic

No. of Samples	Detergent Solution % by wt.			Increased Whiteness Ives %	pH Value	Surface Tension Dynes/cm.
6	0.03 soap			13.6	9.2	31.3
6	0.03 " & .0025 NaOH			14.6	10.2	26.8
6	0.03 " " .005 "			14.2	10.7	27.0
8	0.03 " " .01 "			13.7	11.1	30.2
6	0.03 " " .015 "			14.3	11.3	30.6
6	0.03 " " .02 "			14.4	11.4	33.0
2	0.03 " " .03 "			15.1	11.6	33.4

Table III

Detergent Value, pH, and Surface Tension of Sodium Oleate Solutions with Builders

No. of Samples	Detergent Solution % by wt.				Increased Whiteness Ives %	pH Value	Surface Tension Dynes/cm.
6	0.03	soap			21.1	9.7	27.4
6	0.03	"	& .005	NaOH	18.6	10.7	30.6
6	0.03	"	" .01	"	17.3	11.0	31.5
6	0.03	"	" .02	"	15.4	11.4	31.7
2	0.03	"	" .03	"	13.3	11.6	31.3
6	0.03	"	" .025	S Sil.	17.8	9.7	26.9
6	0.03	"	" .05	" "	17.2	9.8	25.9
6	0.03	"	" .075	" "	16.7	9.8	25.9
2	0.03	"	" .10	" "	16.3	9.9	25.1
6	0.03	"	" .005	M Sil.	16.8	10.0	27.2
6	0.03	"	" .01	" "	16.2	10.4	26.1
6	0.03	"	" .02	" "	16.8	10.6	25.3
2	0.03	"	" .03	" "	13.8	10.9	25.1

Note: All silicates are products of Philadelphia Quartz Company.

Note: S Sil. is the "S" Brand ($Na_2O:SiO_2 = 1:3.86$)
M Sil. is the "Metso" Brand ($Na_2O:SiO_2 = 1:0.97$)

DISCUSSION OF THE DATA

Table I gives the average values of the detergent power, pH value, and surface tension for solutions ranging from zero to 0.20% neutral sodium oleate by weight. Neutral sodium oleate means the compound composed of equivalents of sodium and oleate ions and does not refer to the pH values of its solutions. The pH values increase with the soap concentration except for the 0.12% and the 0.20% soap solutions. Since it is quite easy to secure check results with a hydrogen electrode in dilute alkaline soap solutions, these measurements are considered to be correct for these solutions.

The surface tensions of the neutral soap solutions decrease to approximately two fifths that of the pure water when the solution contains 0.03% soap. The values go slightly lower for the more concentrated solutions, but they are neither constant nor regularly lowered with the increased soap concentrations.

The detergent values of the solutions of neutral sodium oleate are represented numerically in the column

marked "increased whiteness, Ives per cent". The 0.03%
soap solution shows the highest detergent power of any of
the solutions. This value is the same as that determined
by Millard (12) from interfacial tension measurements
against benzene. The data shows that the 0.15% and the
0.10% soap solutions have only slightly better cleansing
powers than the distilled water.

Investigators using other methods for evaluating
detergent effects have found optimum soap concentrations
varying widely. McBain (8) found 4.45% soap to be the
optimum soap concentration for carbon suspension. Fall (4)
gives from 0.20% to 0.40% soap as the concentrations
which suspend manganese dioxide to the greatest extent.
Rhodes and Bascom (23) use, as do many of the later workers,
soap solutions of about 0.25% concentrations. Vincent (21)
found that soap solutions of 0.05% to 0.10% gave emulsions
which were considered to be most stable.

In actual laundry practice, it is customary to use
from 0.05% to 0.10% soap solutions, which concentrations
may be lessened with the addition of alkaline builders.
It may be seen that a large part of the work on soap
solutions has been done with soap concentrations much

greater than those necessary in actual washing operations
where the soil, cloth, and solvent effects must vary very
greatly.

The solutions of soap concentrations greater than
0.03% were poor cleansing agents when the cotton cloth
soiled with carbon black is used to determine cleansing
power. The more concentrated solutions seemed to produce
such a large volume of soap suds during the washes that
the mechanical action was rendered much less effective in
loosening the dirt particles. The mechanical buffering
action probably explains the decreased detergent action
of the solutions above 0.03% soap. It must be realized
that a variation of the acid character of the dirt and
salts capable of rendering the soap inactive will cause a
variation of the optimum soap concentrations. The work
represented in this paper was performed with acid free
dirt, cotton cloth, and distilled water, all of which
makes for reproducible measurements.

Table II shows the detergent value, pH value, and
surface tension measurements of solutions of soap and
caustic, the soap having been made from free oleic acid
produced in an electrodialyzing cell. It was thought,
since the cleansing action is probably closely related to

the colloidal condition of the soap solution, that the traces of inorganic ions present might have some effect upon the solution properties. The sodium oleate as supplied by Merck and Company gave qualitative tests for chloride, sulfate, and potassium ions in addition to sodium. The solution after dialysis failed to give tests for chloride, sulfate, and potassium ions and gave only a very faint line for sodium in the spectroscope. This indicates that the inorganic ions were very materially reduced in concentration.

The pH value of the soap solution without caustic is lower than the value for a 0.03% neutral sodium oleate solution. Probably the method by which the soap was prepared accounts for this low alkalinity. The pH of the solutions increases with the increased caustic concentrations while the surface tension reaches a minimum with the soap solution containing 0.005% caustic. The values for detergent effect are low and show no definite tendency, but give a maximum value with 0.03% caustic.

Table III gives the measured values for neutral sodium oleate solutions to which caustic and two different sodium silicates were added. The silicates were included in the investigation, not in an effort to determine the

value of sodium silicate as a detergent, but to produce
alkali by hydrolysis. Caustic and salts which produce
alkali by hydrolysis are common additions to commercial
soaps. These alkalis improve the detergent effect of soaps
in so far as they are able to neutralize acidic dirt and
prevent the formation of insoluble soap particles.

An examination of the data will show that with caustic
as the builder, the detergent power decreases while the pH
value and the surface tension increases as the builder is
increased in concentration. With S silicate
($Na_2O:SiO_2 = 1:3.86$), the detergent power and the surface
tension decrease while the pH value increases slightly.
With M silicate ($Na_2O:SiO_2 = 1:0.97$), the pH value increases
and the surface tension decreases while the detergent
power seems to have no definite tendency.

It is generally believed that soap solutions are
composed of an equilibrium mixture of simple soap molecules,
the products of ionization and of hydrolysis, and colloidal
soap particles. According to the theory of colloidal
detergency, these colloidal soap particles or ionic micelles
are responsible for most of the cleansing effect of soap
solutions. Since hydroxyl and alkali metal ions are formed
by the soap hydrolysis and ionization, the addition of an

alkali should cause a shift in the equilibrium to give more
soap molecules and more colloidal soap particles. The
point at which the detergent effect is a maximum, according
to Rhodes and Bascom (23), is 10.7 pH. This should mean
that the colloidal properties of the soap solution are at
a maximum at this alkalinity. Fall (4) states that nothing
can take the place of soap itself; that if builders are
added, any cleansing action which they show is shown
because they are taking the place of a certain amount of
soap of greater detergent efficiency.

Any soap solution, according to Snell (19), having a
pH of 10.2 or less is acid to soap. As such, one would
expect the detergent action to be low since there is a
large tendency to form insoluble acid soap particles.
Throughout this work, maximum detergent effects were
produced in solutions whose pH value was below 10.
Apparently acidic soap solutions have real detergent powers.

CONCLUSIONS

Measurements on dilute solutions of sodium oleate
and on sodium oleate solutions to which some of the common
alkaline builders have been added, do not show any direct
relationship between the detergent power as measured, the
pH value, and the surface tension. Consequently, it may
be concluded that in the range studied, the detergent
effect is neither proportional to the pH nor to the surface
tension lowering of the solutions.

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