Comparative Viscosities of Coconut Oil Liquid Soaps[1]

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THE mobility of a liquid soap is an important characteristic for use in filling machines. While the mobility and the viscosity of a liquid may not be synonymous, there is a close relationship when liquids are free from gelation. Since the viscosity of a soap can be taken as an indication of its ease of flow through the pipes and tubing of a filling equipment, a study of viscosities of coconut oil liquid soaps at various temperatures and concentrations was made to obtain this information.

Liquid soaps behave differently physically when their fatty acid components are varied in molecular weight and structure. The present problems are kept from becoming too complex by limiting the kind of liquid soaps to those derived from coconut oil. Potassium soaps of coconut oil and of coconut oil fatty acids were used so that the range of concentration might be varied more widely than if the soaps were made from sodium hydroxide. Also the potassium soaps are the most commonly manufactured and used.

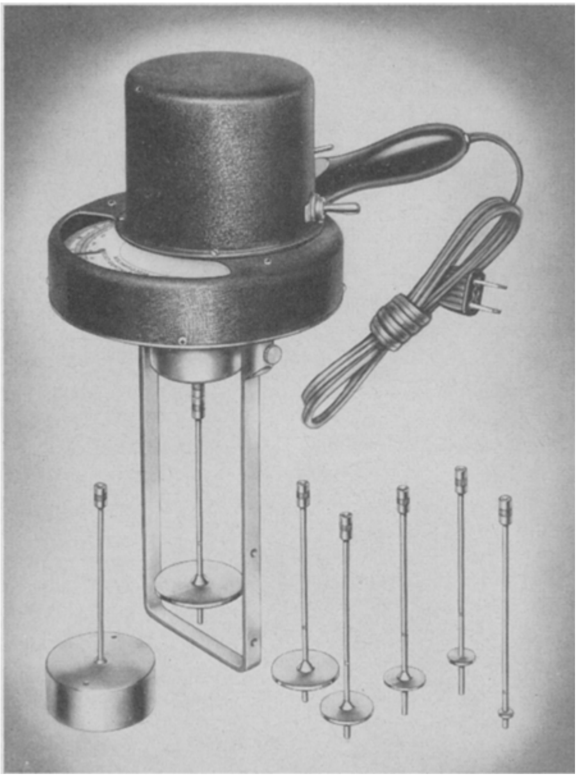

FIG. 1

Apparatus used for obtaining these data was a Brookfield Viscometer shown in Figure 1. Mechanical features of this instrument made this work possible. It is a viscosimeter consisting of a synchronous motor, a spindle or other device that is rotated in the liquid to be examined, a dial, and a pointer. The pointer is connected to the power unit through a calibrated spring. The torsion on the spring is a measure of the shearing force exerted on the liquid by the rotating spindle, and this amount of torsion is a measure of absolute viscosity which can be read upon the scale. There are a number of speeds and spindles and types of stirrers so that one can be chosen to measure the viscosity of any liquid in question as well as to detect non-Newtonian flow properties.

The instrument used for this work was the model (LVF) provided with a spindle guard shown in the diagram Figure 2 and indicated by B. The operating position of the spindle A and of the spindle guard B are indicated by the dotted line. The guard B is fastened into operating position over lugs by a slight turn. Spindle A is attached by threads onto the driving mechanism at C.

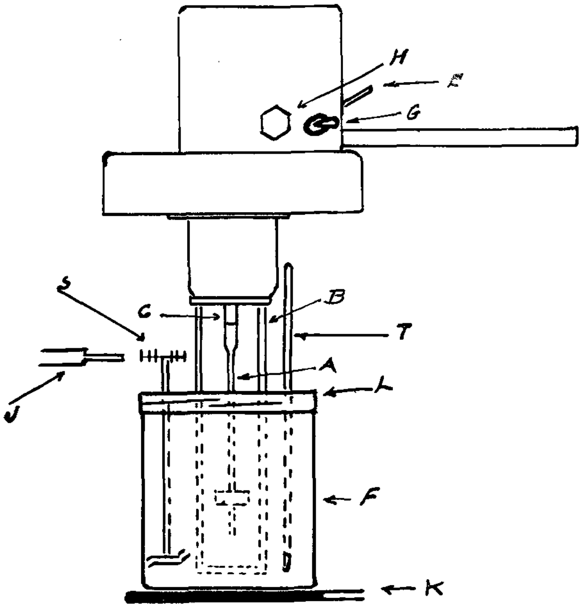

FIG. 2

A speed selector H regulates the RPS of the spindle A. The switch G and the clutch E are indicated in Figure 2. The clutch E is a locking device for protecting the spring from severe initial torque and also for locking the pointer on the dial so that a reading can be taken. More complete description of the apparatus and its scope can be furnished by the manufacturer.

In order to adapt this instrument to the present problem, the spindle guard was detached from its support and inserted through two slots in the lid L of the glass jar F. The spindle A was put through a small hole from below the cover and later screwed into place as shown.

The jar was provided with a thermometer T and a stirring device S. This stirrer was made of glass and provided with a sort of turbine on the upper end. A jet of air directed against the turbine provided adequate agitation of the liquid without causing any vibration. The instrument was held in place by a support on a ring stand. Heat was provided by means of a small hot plate K.

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The jar with lid, spindle guard, and spindle was always detached from the main mechanism prior to each determination, and the jar was unscrewed and all parts were washed and dried before each test. The jar was filled to the required depth with a liquid soap. The lid was then replaced, and the assembly was put into the refrigerator at about zero degrees to cool until the thermometer was at from 1°C. to 2°C. The jar, with soap, was then fastened into operating position. The soap was then stirred for about 30 seconds, and the viscosimeter was set in motion. Usually one minute was allowed for the spindle and the liquid to come to temperature equilibrium, and then a reading was taken. Many readings were taken at 1°C. intervals through the range of from about 5°C. to 20°C. because the greatest rate of change of viscosity occurred during the first 15 degrees. The temperature of the jar and contents were elevated from the lowest temperatures to about 10°C. by merely warming the jar with the hands. Higher temperatures were obtained by intermittently heating with a hot plate. Readings at 5-degree intervals between the temperatures of 20°C. and 60°C. and at 10-degree intervals from 60°C. to 80°C. were found to be sufficient to provide the necessary information for the construction of a graph.

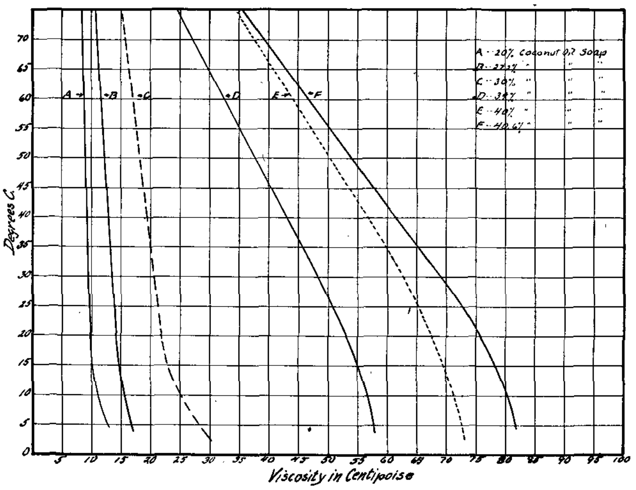

FIG. 3

The study of agreement between repeated runs was made upon two soaps having a 27.2 and 30% dry soap content. Corresponding readings varied from zero to one centipoise. A further study of the operation also shows that less deviation occurred when five minutes or more elapsed between the readings from the lowest temperatures up to 15°C. Some loss of moisture at the higher temperature is a cause of slight error but scarcely discernible in soaps at 30% total solids or less.

The first set of viscosity determinations were made upon liquid soaps whose concentrations, as total solids (non-volatile by oven method), included soaps of these concentrations; 20%, 27.2%, 30%, 39%, 40%, and 40.6%. These soaps were made by diluting the 40.6% material with distilled water. The original 40.6% soap was made in the plant by hot saponification of Manilla grade of coconut oil with potassium hydroxide. It contained the glycerol resulting from the saponification, and the glycerol is included in the values for total solids as is common practice for this kind of soap. The glycerol content of these soaps is very close to 11% of the figure for total solids. The soap was finished at 0.20% free KOH.

These viscosity data are shown in Figure 3 where viscosity in centipoises as abscissae are plotted against the temperature as ordinates.

The line of dashes represents the behavior of a 30% soap, and the dotted line represents the 40% soap. These two curves are chosen for comparison with the other liquid soaps in the graph presented here.

An examination of these curves reveals that at 10° C. (see Figure 3) the viscosity gain between the 20% soap and the 27.2% soap is approximately 0.6 centipoises per 1% increase of soap concentration; from 27.2% to 30% soap the viscosity gain is 3.3 centipoises per 1% in soap concentration; from 30% to 39% soap the viscosity gain is 3.6 centipoises per 1% of increased soap concentration; from 39% to 40% soap the viscosity gain becomes 14.7 centipoises per 1% increase in soap concentration; and from 40% to 40.6% soap the viscosity gain per 1% increase in soap concentration remains about the same at 14.2 centipoises.

The viscosity of soap solutions in water increases with the concentration of the soap, and these changes vary with the kind of soap. Sodium soaps of oleic, palmitic, and stearic acids exhibit differences in viscosities for the same soap concentrations, as shown by the work of Masao Nonaka (1, 2).

Freundlich and Jores (3) report that sodium soaps of stearic acid follow a true viscosity change only up to 0.17% concentration, beyond which a condition of elasticity develops. A similar change occurs with sodium oleate above 2% concentration.

The present work upon potassium soaps of coconut oil gave no indication of deviation from Newtonian behavior under the conditions of the experiments.

The conditions that affect the viscosity of a solution are temperature, concentration of the solute (in this case soap), the molecular weight of the solute, the physical structure of the solute, and, where soaps are concerned, the size of the micelles. Of course, all of these conditions are referred to water as the solvent. These values for the gain in centipoises per 1% increase in soap concentration are shown in Table 1.

TABLE I

Soap Concentration	Gain in Viscosity at 10°C.
20% to 27.2%	0.6 Centipoise per 1% increase of soap
27.2% to 30%	3.3 Centipoise per 1% increase of soap
30% to 39%	3.6 Centipoise per 1% increase of soap
39% to 40%	14.7 Centipoise per 1% increase of soap
40% to 40.6%	14.2 Centipoise per 1% increase of soap

While it has been known that viscosities of liquid soaps increase rapidly with increased concentration, it was not surmised that the viscosity gain was nearly so great as these data show for the difference between a 39% and 40% soap and between 40% and one of slightly higher concentration. All of the viscosities obtained so far were made upon liquid soaps containing the natural glycerol resulting from saponification.

Some of this 40% liquid soap was diluted to approximately 25% concentration and warmed to 50°C. and acidulated, while stirring, with reagent quality hydrochloric acid diluted with 4 parts of water. The acidulation was continued until the water portion indicated acidity in the presence of methyl orange. The fatty acids so liberated were carefully washed free of HCl and salt, and then it was neutralized with potassium hydroxide to yield soap. The amount of liquid soap thus obtained was concentrated by evaporation into portions having 20%, 30%, and 35.6% soap solids. These soaps had no glycerol in their composition as this was washed out in the acid water and the wash water of the previous operation.

Viscosity data were obtained upon these soaps at various temperatures, and curves were constructed which are shown in Figure 4. It can be observed that there is very little difference in the viscosities of a 20% potassium coconut oil soap and 20% potassium coconut oil fatty acid soap. However when the concentration of soap is increased somewhat, the bodying action of glycerol becomes evident. For example, curve H represents a 30% coconut oil fatty acid soap. Comparing this with curve C, the 30% coconut oil soap, the latter has about 5 centipoises greater viscosity. These two soaps are compared on the usual dry or total solids basis. Actually, the soap, as combined fatty acids in soap C, is only 26.7%. The greater viscosity of this soap is due to the presence of glycerol.

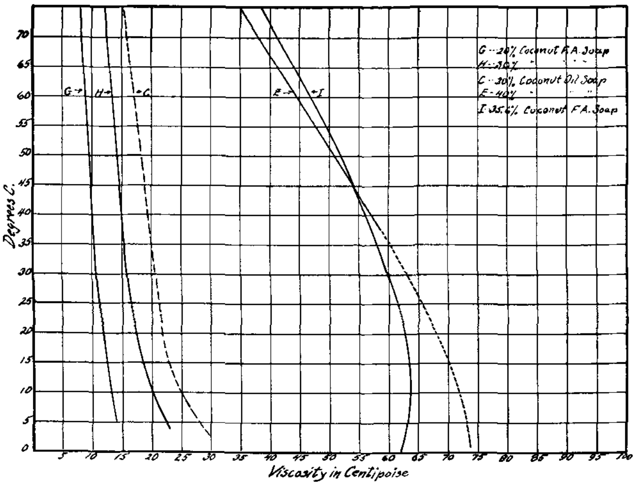

FIG. 4

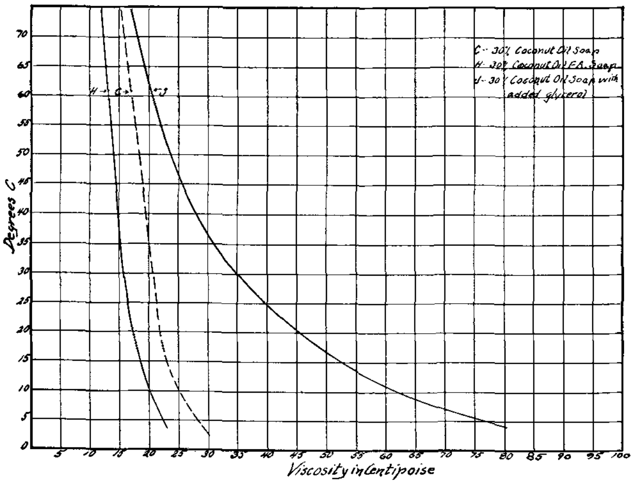

FIG. 5

Curve 1 in Figure 4 represents the potassium coconut oil fatty acid soap, having 35.6% total solids. It has exactly the same amount of combined fatty acids as the soap for curve E, the standard 40% liquid soap. Again, the bodying action of glycerol in liquid soap composition is obvious.

Figure 5 shows graphically what happens when additional glycerine is added to a liquid soap. The soaps represented by curves C and J have 26.7% of combined fatty acids. Curve C represents a standard 30% liquid potash soap. A 40% soap containing glycerol and 35.6% of combined fatty acids was reduced to a 26.7% combined fatty acid soap (like C) by adding additional glycerol. This is done sometimes to gain transparency. Again we see that the viscosity of the liquid soap is almost doubled in the temperature range that the soap generally is used. The regular 40% liquid coconut oil soap has a higher viscosity than sales appeal demands. A decrease in this viscosity is not injurious to the appearance of the product and facilitates the handling of the soap in the plant. This improvement can be gained by the addition of salts, one of which is potassium chloride. The addition of potassium chloride has been recognized as being beneficial in reducing the viscosity of a liquid soap, but the real gain had not been recognized until the viscosity of these treated liquid soaps had been determined. Curve K, Figure 6, shows that a great reduction in viscosity is obtained; the viscosity drop amounted to about 25 centipoises. This soap is very acceptable, having total solids of 40%, of which only 0.5% is potassium chloride. A still further gain in quality and ease of handling comes from adding 0.50% sodium salt of ethylenediaminetetra acetic acid, commonly called a chelating agent. This addition, shown by curve L, Figure 6, not only reduced the viscosity of the soap but also enhances its appearance and its detergent properties and may be well called an active and useful additive. The presence of 0.50% of EDTAA salt reduces the viscosity of the usual 40% liquid soap by about 33%.

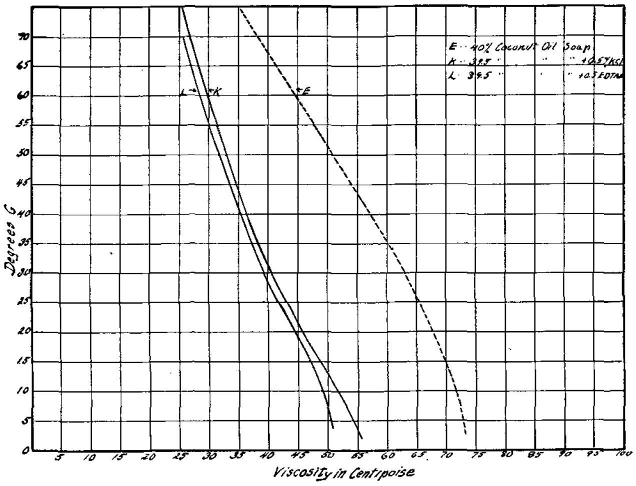

FIG. 6

At concentrations above 41 to 42% potassium soaps of coconut oil (including glycerol) begin to gel, and at about 43.5% total solids they become a firm gel. The gel is so firm that the soap has a "ring" when struck. Soap in this condition is termed "crystal" or "crystal base." Liquid potash soap made from coconut oil fatty acids and free from glycerol begins to gel at about 37.5% and is a firm crystal base at 40.5% concentration. Hence a glycerol-free crystal base has less total solids by oven dry test than one made from coconut oils, but the two are practically equal in the amount of combined fatty acids.

These gelled soaps of the crystal type have some peculiar properties. They are liquid when hot and solid when cold. They remain in the crystal state through the range of useful temperatures from about 5°C. to 80°C. When the crystal base type of soap is cooled to a low temperature, these soaps again liquefy and become quite thin. Liquid soaps that are so concentrated that they are passing from the liquid state to the crystal state first become thick and viscous but upon chilling return to a thinner liquid. For the present it is assumed that this condition explains the reversal in the viscosity of a liquid soap, curve 1, below 15°C. (Figure 4).

REFERENCES

1. Masao Nonaka, J. Soc. Chem. Ind., Japan, *30*, 221-225, 828-835 (1927).
2. *Ibid.*
3. Freundlich and Jores, Kolloidchem. Beihefte, *22*, 16-37 (1926).

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Methanolysis of Triglycerides by an Anion Exchange Resin[1]

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IN a preparation of radioactive glycerol (1) Amberlite IRA-400-OH was used to liberate the carbon-labelled glycerol from dicaproin. The reaction was carried out in methanol, and the water-soaked resin provided more than the amount of water required for the hydrolysis. In addition to the free glycerol a large amount of methyl caproate was found, indicating that interesterification had occurred rather than the expected saponification.

Catalysis by cation exchange resins in esterification, interesterification, and saponification has drawn considerable attention recently (2, 3, 4). Interesterification by anion exchange resins, to our knowledge, has not been reported. In addition to any possible preparative value it seemed to be desirable to learn more about the effect of anion exchange resins upon fats for anion exchange resins have already proven to be of value in the analytical phase of metabolic studies (5).

Two detailed experiments were conducted on cottonseed oil, identical in all respects except that the same catalyst resin recovered from the first experiment was used in the second experiment rather than fresh resin. Cottonseed oil, 55 g., was dissolved in 250 ml. ether plus 250 ml. ethanol. When 20 g. of moist Amberlite IRA-400-OH-AG resin were added to the solution, two liquid layers formed. As the reaction proceeded, the liquid again became homogeneous. After three days' shaking the resin was filtered off and washed with the same solvent. When the sample was reduced to dryness under nitrogen, the oil contained some large drops of glycerol. Free glycerol and monoglyceride were determined according to the procedure of Pohle and Mehlenbacher (6) on the aqueous extract of this mixture and upon the residual oil. Total bound glycerol was determined by periodate titration after saponification of the oil and separation of the fatty acids from the glycerol (7). Blanks run with methyl palmitate gave negligible values. The recovery of oil was 52.9 and 53.9 g. in the two experiments. The analytical results are listed in Table I. Probably the interesterification proceeds stepwise. The periodate values however were raised only slightly from 0.071 meq. per g. cottonseed oil to 0.098 and 0.090 meq. per g. interesterified oil, indicating that under the above conditions the larger portion of acids not converted to methyl esters remained as tri- and diglycerides. Since the method of determining the total bound glycerol does not give account of partial interesterification, the values calculated on that basis are minimum values. It seems justifiable to base this calculation on the residual bound glycerol rather than on the recovered free glycerol. The amount of glycerol held back by the resin has not been determined, and the increase of both free and bound glycerol in the second experiment would be explained by such effect.

TABLE I

Methanolysis of Cottonseed Oil by Amberlite IRA-400-OH-AG

	Mg. Free Glycerol per g. Oil	Mg. Bound Glycerol per g. Oil	Minimum Interesterification
			%
Cottonseed Oil	......	108.2, 104.5	....
Interesterified			
Mixture I	69.5	16.9, 17.3	84
Mixture II	75.0	30.2, 29.5	72

Free fatty acids were found only in the resin. After the second catalysis the resin was shaken with aqueous hydrochloric acid and ether for several hours, and 0.89 g. of a semisolid oil was obtained, having an acid value of 166. The capacity of 20 g. of resin at saturation is about 6.9 g. stearic acid.

In other experiments corn oil, coconut oil, and cod liver oil were treated. The interesterified oils were analyzed for bound glycerol only, calculating therefrom the percentage of interesterification. The re-

TABLE II

Alcoholysis of Triglycerides

Oil	Solvent	Resin Wt.	Time	Interesterification
			hrs.	%
Cottonseed 50 g.	Methanol, Skelly B.	20 g.	48	73
Corn 45 g.	Ethanol, ether	20 g.	72	61
Cod liver 50 g.	Methanol, ether	20 g.	48	67
Coconut 50 g.	Methanol, Skelly B.	20 g.	48	74

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