with ammonium hydroxid, being careful to keep the specific gravity above 1.09. By the conductivity method it was found that 25.9 cc. of a 5 per cent solution of ammonium hydroxid were required to neutralize 1000 cc. of the solution and by the titration method 25.95 cc. were required. With another citrate solution 35.4 cc. of a 5 per cent solution of ammonium hydroxid were required per liter by the conductivity method and 35.6 cc. by the titration method.

We next determined by the titration method the amount of citric acid and ammonia contained in one liter of a strictly neutral solution of ammonium citrate, of exactly 1.09 specific gravity, with the following results:

- 1 cc. citrate sol. gave 26.34 cc. $N/10$ NH_3 ,
- 1 cc. citrate sol. gave 26.33 cc. $N/10$ $C_6H_8O_7$,
equivalent to 44.76 grams NH_3 per liter
equivalent to 168.57 grams $C_6H_8O_7$ per liter
Ratio of NH_3 to $C_6H_8O_7$ = 1 : 3.766.

The three solutions claimed to be neutral by McCandless contained 44.3 grams NH_3 and 168.76 grams $C_6H_8O_7$ per liter, the ratio being 1 : 3.809. The results obtained by us conclusively prove that such a solution would be slightly acid, which fact is further substantiated by the ratio of ammonia to anhydrous citric acid being too wide.

SUMMARY

The titration method of preparing neutral ammonium citrate solutions is accurate and easy of manipulation.

It establishes beyond a doubt that the ratio of ammonia to anhydrous citric acid in the neutral solution should be 1 : 3.765 and that one liter of 1.09 specific gravity should contain 44.76 grams NH_3 and 168.57 grams $C_6H_8O_7$.

The titration method affords a simple means of comparing ammonium citrate solutions made in different laboratories.

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THE FLUIDITY OF BUTTER FAT AND ITS SUBSTITUTES

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The study of the viscosities of butter fat and oleomargarine as a problem of more or less interest, has already been taken up by several investigators with different methods of approach and different types of viscosimeters. Wender¹ worked with an instrument of the Ostwald class, modified so that, according to his statement, it could be cleaned with greater speed and ease. The Reichert-Meissl number of each sample was taken as a measure of purity. The fats were dissolved in chloroform, the viscosity of the solvent being taken into consideration. Wender found that the viscosity of oleomargarine was always greater than that of butter and with both decreased with rise in temperature, but did not change on standing for a considerable length of time. Further, although the viscosities of the butter fats were fairly constant, there were appreciable differences in the margarines from different sources. The amount of mar-

garine added could be approximately determined.

Killing² contributed nothing new in his study of the viscosities of butter and other fats, and his apparatus was so crude that no advance was made.

Raffo and Foresti,³ in an article on a "New Method for the Determination of Margarine in Butter," describe results obtained by an Ostwald instrument. They used butter from two sources and took the viscosities at 50° C. of the fats obtained by melting and filtering from curd and water. The time of flow was found to increase as the percentage of oleo fat increased, different samples giving concordant results. Their data indicate roughly that the viscosity is some function of the composition, but what particular function is not stated.

It is evident that any connection between the viscosity and the composition of butter fats, if it exists, has not been clearly and definitely established. A study of this important relation should therefore reveal by the use of accurate methods of analysis, results of especial value and interest. It is our purpose in this article to present the results of a series of viscosity measurements of various butter and oleomargarine samples, and of mixtures of these of known composition. By utilizing a viscosimeter which enabled us to express viscosities in absolute units, a definite standard of comparison may be adopted. Such measurements are entirely independent of the apparatus employed, and the "times of flow," which are recorded in so many works of this nature and which mean nothing to anyone else than the observer and his particular viscosimeter, do not need to be considered.

We prepared our samples, obtained from various sources, by melting at the lowest possible temperature and allowing to stand for two or three hours in that condition. The curd and water settled to the bottom leaving the clear supernatant fat which was decanted through a filter. The following constants were taken: the iodine number which shows the amount of unsaturated acids present, the saponification number, the percentage of soluble and insoluble acids, the volatile acids, the densities at 40°, 65°, and 90° C., and the viscosities at intervals of 10° from 40° to 90° C. These constants, while by no means representing a complete analysis, give a very definite idea of the purity and the composition of the fat examined.

The iodine number was obtained by treating about one-half a gram of fat with 50 cc. of Hübl's solution (mercuric chloride and iodine in alcohol), and titrating the remaining iodine with sodium thiosulfate solution after three hours' standing to ensure complete absorption. The number is expressed in the percentage of iodine absorbed, *i. e.*, the number of grams of iodine taken up by 100 grams of fat.

The saponification was carried out with an alcoholic potassium hydroxide solution, the mixture being heated on the water bath with a reflux condenser for thirty minutes, and the excess alkali then titrated with half-normal hydrochloric acid. The saponification (Koettstorfer) number is expressed as milligrams

¹ *J. Am. Chem. Soc.*, **17**, 719 (1895).

² *Z. angew. Chem.*, **1894**, 643; **1895**, 102. *J. Soc. Chem. Ind.*, **1895**, 198.

³ *Gazz. chim. ital.*, **39**, 441 (1911).

of potassium hydroxide required to saponify 1 gram of fat. After the titration, 1 cc. exceeding the exact amount of half normal hydrochloric acid necessary to free the fatty acids was added. The insoluble acids, after cooling, were washed free from the soluble acids and the latter titrated with decinormal alkali, the result being calculated as per cent butyric acid. The cake of insoluble acids was dried and weighed and the per cent calculated.

To obtain the Reichert-Meissl number, which is perhaps the most important of these constants, about 5 grams of fat were saponified by heating under pressure with caustic soda and 95 per cent alcohol. Sulfuric acid in sufficient amount to free the fatty acids was added and the whole again heated under pressure. The flask was then connected with a condenser, the volatile acids distilled off, and an aliquot portion titrated with decinormal alkali after filtering. The result signifies the number of cubic centimeters of decinormal potassium hydroxide solution required to neutralize the volatile acids obtained from 5 grams of fat.

The densities of the samples were taken in an ordinary Ostwald pycnometer, comparison being made with the density of water at 4° C.

Of particular interest to us in our study of the viscosity of these very viscous liquids is the work of Scarpa,¹ who, discerning the sources of error in the viscosimeters of various types, devised one of very great accuracy and which was capable of wide application. In his instrument there was a capillary tube from 5 to 10 cm. long and about 0.2 mm. inside diameter. The lower end of the vertical capillary dipped into a test tube containing oil; the upper end was joined to a series of bulbs of varying volume. At the top it was connected to an apparatus for maintaining reduced pressure, and also with a manometer. The whole was put under diminished pressure and the liquid drawn up to fill one or more of the bulbs, the amount so drawn through the capillary depending on the viscosity. The time t_1 was observed. By use of one or more bulbs the times of flow of liquids of very different viscosities were not widely divergent. The liquid was next allowed to flow back under its own weight and atmospheric pressure, taking the time t_2 . The viscosity is proportional to the ratio $t_1 t_2 / (t_1 + t_2)$. The constant of proportionality is dependent neither upon the surface tension nor the quantity of the liquid. A characteristic value for the proportionality constant could be obtained by using the instrument under the same reduced pressure. By determining $t_1 t_2 / (t_1 + t_2)$ with the same quantity of liquid at the same temperature, relative results could be obtained. Values obtained by the Scarpa and Engler instruments were very widely divergent, the former being by far the more consistent, especially with very viscous oils.

While Scarpa's viscosimeter is evidently one of considerable efficiency, we believe that the instrument described by one of us,² and which has been applied to a study of various liquids,³ presents to a

greater degree the advantage of facility of manipulation combined with great accuracy. As do the viscosimeters of Thorpe and Rodger,⁴ and Bingham and White,⁵ it gives viscosity results in absolute units which are corrected for the gain in kinetic energy involved in the flow of the liquid through the capillary tube. By its symmetrical shape there is only a small correction to the pressure as measured in the manometer. Finally, by varying the pressure, fluid and viscous liquids may be measured in the same instrument and at all temperatures.

Since the viscosimeter has been described in detail in previous articles³ and has been modified in only one respect for this work, a very brief description will suffice. It consists (Fig. 1) of two vertical glass limbs as nearly alike as possible, except for there being a trap in one, these limbs being connected by a horizontal capillary tube fused into their lower ends. The capillary is of about 0.1 mm. internal diameter and of a length suited to the nature of the liquids to be investigated. On one limb two marks are so placed that, in falling from the higher to the lower, from 2 to 4 cc. of liquid passes through the capillary. This volume is determined before the viscosimeter is put together. Above the higher mark there is a trap. On the other limb, not far above the capillary, another mark is etched. The volume of liquid used is always the amount required to fill the instrument from this last mark to the top of the trap in the other limb.

The modification of the viscosimeters previously used, though only slight, has made the instrument easier to make and to calibrate. In this work, instead of calibrating two limbs, we have taken the time of falling from the higher to the lower mark, *VISCOMETER B* then reversing the pressure, taking the time of rising between the same marks. This has proved as satisfactory as the former method and saves the calibration of one limb.

The following formula was used in the calibration of the viscosity results:

$$\eta = \frac{\pi r^4 p t}{8 v l} - \frac{v d}{8 \pi l}$$

η is the viscosity, r the radius, l the length of the capillary, v the volume of liquid passing through the capillary, d the density of the liquid, p the pressure, and t the time of flow. The constants $\pi r^4 / 8 v l$ and $v / 8 \pi l$ were determined by taking the time of flow of water at 30° and a suitable pressure, the value of η being taken from the data of Thorpe and Rodger. The correction to the pressure for any asymmetry in the instrument has an opposite effect according to

¹ Gazz. chim. ital., 40, II, 261 (1911).

² Biochem. Z., 37, 482 (1911).

³ THIS JOURNAL, 4, 106, 267, 878 (1912).

⁴ Phil. Trans. London, (A), 185, 397 (1894).

⁵ Z. physik. Chem., 80, 670 (1912).

⁶ Loc. cit.

whether the liquid is rising or falling in a certain (the calibrated) limb. If p_1 and t_1 , and p_2 and t_2 , represent the times of flow and the pressures when the liquid is rising and falling, respectively, or *vice versa*, the correction to the pressure x may be calculated according to the equation

$$x = \frac{p_1 t_1 - p_2 t_2}{t_1 + t_2}$$

may be suspected. Of course an adulterated butter may be made more fluid by the addition of one of many oils possible, and such admixtures could be detected only by a determination of other constants.

That the better grades of butter are the less viscous is evidenced by the constants of the four samples studied. Sample I has the least amount of soluble and volatile acids, and its high viscosity corresponds

Sample	Iodine number			Saponification number			Insoluble acids			Soluble acids			Reichert-Meissl No.
	I	II	Av.	I	II	Av.	I	II	Av.	I	II	Av.	
Butter I.....	36.95	37.13	37.04	228.9	229.1	229.0	89.41	89.60	89.51	3.421	3.481	3.451	25.16
Butter II.....	38.10	37.92	38.01	224.1	225.0	224.6	88.47	88.92	88.70	3.869	3.911	3.890	26.69
Butter III.....	30.90	31.02	30.96	231.3	231.5	231.4	89.23	89.14	89.18	4.017	...	4.017	27.04
Butter IV.....	34.07	34.26	34.17	230.4	230.1	230.3	88.71	89.10	88.91	4.026	...	4.026	27.08
Oleomargarine I.....	58.77	59.17	58.97	194.9	195.3	195.1	94.74	95.04	94.89	0.1	1.1	0.1	0.1660
Oleomargarine II.....	64.15	64.92	64.54	191.3	190.9	191.1	94.75	...	94.75	Less than	...	0.1	1.100
Oleomargarine III.....	67.92	67.92	67.92	136.3	136.9	136.6	93.48	93.41	93.44	Less than	...	0.1	0.9124
Oleomargarine IV.....	78.43	78.06	78.25	134.6	133.8	134.2	98.06	97.99	98.03	Less than	...	0.1	0.4989
Butter II (stale).....	40.35	40.19	40.27	227.3	226.9	227.1	89.27	89.33	89.30	4.175	4.163	4.169	9.736
Butter III (stale).....	33.44	33.74	33.59	233.4	233.6	233.5	89.48	89.60	89.54	3.749	3.741	3.745	26.01

While one viscosimeter may be used for many liquids, where a long series of measurements are to be made with substances of similar viscosity it is more practicable to construct one which will allow reasonable times of flow. Therefore, for the measurement of these fats, a viscosimeter was constructed with a very short capillary tube, and its constants were determined by using a glycerol-water mixture, the viscosity of which was measured in an instrument adapted to liquids of the viscosity of water, and having a correspondingly longer capillary tube.

Calibration of the viscosimeter used for the fats gave the following results:

Length of capillary (approx.).....	1.8 cm.
Volume of liquid passing through the capillary.....	2.76 cc.
Pressure correction.....	±0.20 cm.
$\frac{\pi r^4}{8 \eta l}$	0.000004916
$v/8 \pi l$	0.03286

The times of flow for the various fats and at different temperatures varied from about ten to two minutes.

The results are given in the tables which follow. Together with the viscosities are presented the fluidities, these latter being calculated by taking the reciprocals of the average viscosities. All viscosity results are expressed in C. G. S. units.

From the results given in the tables several conclusions may be drawn. In the first place, as would be expected from the fact that oleomargarine is more largely made up of the glycerides of the higher aliphatic acids, the margarines are considerably more viscous than butter. Wender¹ seemed to consider that there was but little variation in the viscosity of different butter samples, while the viscosities of margarines from various sources differed widely. This work, however, shows that an accurate instrument can detect variations in different grades of both products, and that slight changes in composition affect the viscosity of these fats to as marked an extent as they do the other constants determined. In general, the lower the viscosity the purer is the butter, and if a high viscosity is found, adulteration by beef or other fats

to the fact that it is the poorest sample. Samples III and IV have the lowest viscosity and are shown to be the best butters by their high content of soluble and volatile acids.¹

TABLE II—DENSITIES

Sample	40° C.	65° C.	90° C.
Butter I.....	0.9063	0.8901	0.8745
Butter II.....	0.9053	0.8896	0.8722
Butter III.....	0.9026	0.8865	0.8716
Butter IV.....	0.9026	0.8859	0.8720
Oleomargarine I.....	0.9026	0.8894	0.8711
Oleomargarine II.....	0.8989	0.8837	0.8666
Oleomargarine III.....	0.8997	0.8853	0.8666
Oleomargarine IV.....	0.9024	0.8867	0.8682
Butter II (stale).....	0.9069	0.8890	0.8730
Butter III (stale).....	0.9061	0.8992	0.8720

In connection with the change of butter on standing several interesting observations were made. If the butter fat was separated from water and curd, it became rancid very slowly, and after standing for considerable time at room temperature no appreciable change in viscosity could be detected. Consequently some of Samples II and III were allowed to grow rancid before removing the water and curd. The former stood about two months and the latter as many weeks. As shown in Table II, the samples which stood the longer decreased in viscosity, while the others

TABLE III—VISCOSITY RESULTS AT 40°

Sample(a)	Viscosity			Fluidity
	Down	Up	Av.	
Butter I.....	0.3244	0.3249	0.3247	3.080
Butter II.....	0.3228	0.3211	0.3219	3.107
Butter III.....	0.3080	0.3092	0.3086	3.241
Butter IV.....	0.3024	0.3025	0.3025	3.306
Oleomargarine I.....	0.3576	0.3605	0.3591	2.785
Oleomargarine II.....	0.3582	0.3584	0.3583	2.791
Oleomargarine III.....	0.3476	0.3464	0.3470	2.882
Oleomargarine IV.....	0.3352	0.3353	0.3353	2.982
Butter II (stale).....	0.3177	0.3171	0.3174	3.151
Butter III (stale).....	0.3105	0.3111	0.3108	3.218

(a) Butter samples I and II cost 33 cents a pound; III, 38 cents; IV, 30 cents. Oleomargarine samples I, II and III, 25 cents; and IV, 15 cents, increased. From the Reichert-Meissl number it is evident that Sample II lost considerably more of its volatile acids than Sample III. This seeming dis-

¹ It may be noted that Sample IV, purchased in the same market as Sample III at less cost, is shown to be the better of the two.

¹ Loc. cit.

crepancy may be accounted for in the following manner: The butter which was kept for the shorter interval of time gave off some of its volatile acids due to hydrolysis, and the higher acids remained for the most part unchanged. This would increase the relative per cent of these higher acids and consequently the viscosity. The other sample, which became very stale and of a pasty consistency, lost much more of the volatile acids as shown by the constant and we should expect its viscosity to be so much the

TABLE IV—BUTTER-OLEOMARGARINE MIXTURES—I

C. temp.	Viscosity 100 Per cent Butter			Fluidity
	Down	Up	Av.	
40°.....	0.3244	0.3249	0.3247	3.080
50°.....	0.2289	0.2292	0.2291	4.365
60°.....	0.1666	0.1667	0.1667	5.999
70°.....	0.1257	0.1258	0.1258	7.949
80°.....	0.09817	0.09816	0.09817	10.19
90°.....	0.07847	0.07857	0.07852	12.74
95 Per cent Butter				
40°.....	0.3278	0.3262	0.3270	3.059
50°.....	0.2303	0.2296	0.2300	4.348
60°.....	0.1677	0.1678	0.1678	5.964
70°.....	0.1265	0.1264	0.1265	7.905
80°.....	0.09881	0.09858	0.09870	10.14
90°.....	0.07863	0.07891	0.07877	12.70
90 Per cent Butter				
40°.....	0.3268	0.3269	0.3269	3.059
50°.....	0.2303	0.2302	0.2303	4.342
60°.....	0.1684	0.1680	0.1682	5.946
70°.....	0.1275	0.1283	0.1279	7.818
80°.....	0.09889	0.09847	0.09868	10.14
90°.....	0.07946	0.07946	0.07946	12.59
75 Per cent Butter				
40°.....	0.3326	0.3323	0.3325	3.008
50°.....	0.2340	0.2343	0.2342	4.270
60°.....	0.1707	0.1709	0.1708	5.856
70°.....	0.1292	0.1290	0.1291	7.747
80°.....	0.1009	0.1011	0.1010	9.902
90°.....	0.08094	0.08088	0.08091	12.36
50 Per cent Butter				
40°.....	0.3403	0.3381	0.3392	2.947
50°.....	0.2391	0.2404	0.2398	4.170
60°.....	0.1756	0.1745	0.1751	5.712
70°.....	0.1346	0.1350	0.1348	7.418
80°.....	0.1033	0.1035	0.1034	9.672
90°.....	0.08310	0.08277	0.08291	12.06
25 Per cent Butter				
40°.....	0.3484	0.3481	0.3483	2.871
50°.....	0.2465	0.2475	0.2470	4.049
60°.....	0.1796	0.1800	0.1798	5.560
70°.....	0.1369	0.1369	0.1369	7.305
80°.....	0.1071	0.1062	0.1067	9.371
90°.....	0.08556	0.08548	0.08552	11.69
100 Per cent Oleomargarine				
40°.....	0.3576	0.3605	0.3591	2.785
50°.....	0.2520	0.2522	0.2521	3.976
60°.....	0.1844	0.1843	0.1844	5.424
70°.....	0.1398	0.1396	0.1397	7.157
80°.....	0.1094	0.1093	0.1094	9.139
90°.....	0.08758	0.08758	0.08758	11.42

greater. However, putrefaction of the casein also had commenced with a resulting change in the butter fat which lowered its viscosity without increasing the amount of volatile acids. These products, which do not influence the amount of volatile and soluble acids, may be acids of lower molecular weight than those from which they are derived, but which are insoluble and non-volatile. It should be noted that there is an increase in the quantity of insoluble acids in this last sample considered.

If the above inferences are correct, it is very probable that the viscosity of butter increases with time to a maximum, and then decreases on putrefaction. The suggestion is of sufficient interest to warrant further investigation.

The viscosity results in general bear out Bingham's views concerning the relations between viscosity and

TABLE V—BUTTER-OLEOMARGARINE MIXTURES—II

C. Temp.	Viscosity 100 Per cent Butter			Fluidity
	Down	Up	Av.	
40°.....	0.3228	0.3211	0.3219	3.107
50°.....	0.2260	0.2264	0.2262	4.421
60°.....	0.1639	0.1643	0.1641	6.094
70°.....	0.1243	0.1245	0.1244	8.039
80°.....	0.09727	0.09686	0.09707	10.30
90°.....	0.07827	0.07838	0.07827	12.77
40°.....	0.3225	0.3226	0.3226	3.099
95 Per cent Butter				
40°.....	0.3239	0.3227	0.3233	3.093
50°.....	0.2274	0.2278	0.2276	4.393
60°.....	0.1657	0.1660	0.1659	6.027
70°.....	0.1249	0.1253	0.1251	7.995
80°.....	0.09782	0.09714	0.09748	10.26
90°.....	0.07791	0.07818	0.07805	12.81
90 Per cent Butter				
40°.....	0.3242	0.3255	0.3249	3.078
50°.....	0.2289	0.2298	0.2294	4.359
60°.....	0.1667	0.1674	0.1671	5.984
70°.....	0.1265	0.1266	0.1266	7.898
80°.....	0.09884	0.09889	0.09887	10.11
90°.....	0.07900	0.07897	0.07899	12.66
75 Per cent Butter				
40°.....	0.3297	0.3315	0.3306	3.025
50°.....	0.2323	0.2325	0.2324	4.303
60°.....	0.1700	0.1703	0.1702	5.874
70°.....	0.1283	0.1284	0.1284	7.787
80°.....	0.1003	0.0999	0.1001	9.990
90°.....	0.08049	0.08056	0.08053	12.42
50 Per cent Butter				
40°.....	0.3397	0.3401	0.3399	2.940
50°.....	0.2400	0.2408	0.2404	4.160
60°.....	0.1751	0.1755	0.1753	5.704
70°.....	0.1326	0.1327	0.1327	7.529
80°.....	0.1029	0.1028	0.1029	9.817
90°.....	0.08282	0.08274	0.08278	12.08
25 Per cent Butter				
40°.....	0.3486	0.3488	0.3487	2.868
50°.....	0.2460	0.2471	0.2466	4.055
60°.....	0.1814	0.1805	0.1810	5.525
70°.....	0.1375	0.1383	0.1379	7.251
80°.....	0.1062	0.1063	0.1063	9.407
90°.....	0.08576	0.08537	0.08557	11.69
100 Per cent Oleomargarine				
40°.....	0.3582	0.3584	0.3583	2.791
50°.....	0.2535	0.2541	0.2538	3.940
60°.....	0.1833	0.1833	0.1836	5.447
70°.....	0.1391	0.1391	0.1391	7.189
80°.....	0.1087	0.1085	0.1086	9.208
90°.....	0.08747	0.08743	0.08745	11.43

fluidity and composition. Briefly his hypothesis requires that the fluidity of absolutely unassociated liquids, which do not change on being heated, is a linear function of the temperature, and that mixtures of such liquids which do not interact should have additive fluidities. The fluidity temperature curves for one series of mixtures of butter and oleomargarine are shown graphically in Fig. II. It may be noted that they are nearly linear but that the slight curvature

indicates a certain amount of association in the fats. That this curvature is not a result of chemical change of the fats as they are heated from 40° to 90° is proven by the data in Table V. The viscosity of the pure

FIG. II. Fluidity Temperature Curves of Butter-Oleomargarine Mixtures—I

butter was determined after it had been so heated, and there is no change except what is well within the experimental error. Such association in the fats is very possible since it has been shown that esters are more or less associated. This same effect has been noted by one of us in work on fish oils.¹ By Fig. III it is seen that in accordance with the second part of the fluidity hypothesis as stated, the fluidities of the butter and oleomargarine mixtures are additive. Evidently then, any such association as was indicated is so insignificant as regards our results and conclusions concerning the additivity of the fluidities of these fats that it may be entirely disregarded. The slopes of the fluidity-temperature curves are practically identical, and it is safe to conclude that, in this case,

¹ *Loc. cit.*

the fluidity is a linear function of the composition at any and all temperatures. Since the fluidity is the reciprocal of the viscosity it would be generally impossible, according to the theory, for viscosities to be additive. The viscosity curves for the mixtures given

FIG. III. Fluidity Curves of Butter-Oleomargarine Mixtures, 40°

in Fig. IV show that this is also borne out experimentally, for very evidently a linear curve is not obtained. However, as has been repeatedly shown, when the viscosities of such viscous liquids as these fats are studied, no great divergence from the additive relationship is noticed when the viscosities of the

FIG. IV. Viscosity Curves of Butter-Oleomargarine Mixtures, 40°

components of the mixtures approximate each other.

It was stated above that there was some variation in the viscosities of both butter and oleomargarine,

yet there is a certain reliable mean value for both. These values, with the fluidities, are:

	η	φ
Butter.....	0.3200	3.125
Oleomargarine.....	0.3500	2.857

An adulteration of 10 per cent margarine in butter could be readily detected in the apparatus used in any case. Since pure butters from any one creamery vary very little, by finding the mean value for such products, admixture of a foreign fat of different viscosity could be shown if even only 1 per cent were so added.

SUMMARY

1. Oleomargarine fats are always more viscous than butter fats except, of course, where the viscosity of the former is greatly lowered by the introduction of large amounts of liquid fats as indicated by a chemical analysis.

2. On standing, the viscosity of butter probably increases to a maximum due to a loss of volatile acids, and then becomes less viscous as putrefaction sets in.

3. Although the viscosities for both fats vary somewhat in products from different sources, the fluctuation is always about a mean value which might be assumed without great error as a standard.

4. The viscosities of the mixtures are not strictly additive.

5. The fluidities are practically linear functions of the temperature.

6. The fluidities of the mixtures are additive, so that these, and not viscosities, should be the basis for any comparison.

7. Assuming that the fluidity of butter does not vary more than 5 per cent in value, an adulteration of 10 per cent oleomargarine can be detected with assurance by the method of determination used.

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THE PROPERTIES OF WATERED MILK

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Much work in the detection of added water in milk has been done by the usual chemical methods. So far as the authors are aware, no extensive studies have been made of the changes met where hard well water instead of distilled water has been added to milk, or where sucrose has been added to watered milk to build up the refractometer reading, or where additions of sucrose have been made to whole milk serum to build up the immersion refractometer reading.

The standard composition of milk has been well established, and published results of numerous analyses of American cow's milk are well known.¹ In recent years the method of detecting watered milk has been largely a study of the deportment of the given sample of milk when the corresponding milk serum was prepared and examined with the Zeiss immersion refractometer. Various methods have been suggested

for the preparation of the milk serum prior to the examination of the refractive power of the serum. Villiers and Bertault,^{2,3} as early as 1898, devised a method using acetic acid for the removal of milk proteins. Matthes and Müller,³ in 1903, made use of the Zeiss immersion refractometer for the examination of the serum which they obtained from spontaneously soured milk. Leach and Lythgoe,⁴ in 1904, made use of the immersion refractometer in examining milk serum prepared by the Woodman method. To 100 cc. of milk at about 20° C., 2 cc. of 25 per cent acetic acid were added, well mixed and placed on a water bath at 70° C. for 20 minutes. The mixture was then cooled for 10 minutes in ice water and filtered. The main difference between their method and those formerly used was in the heating of the acid-milk mixture for longer times at lower temperatures prior to filtration. Baier and Neumann⁵ used an asapol-citric acid mixture as the precipitating agent. The serum so prepared was examined with the Wollny milk fat refractometer. Ackermann⁶ used calcium chloride as the precipitating agent in the preparation of milk sera. With so many procedures available, it seemed desirable to compare the various methods on samples of known purity. This was done by Lythgoe and Nurenberg.⁷ They found some methods had certain advantages over other methods but for ease of manipulation and getting concordant results, the Woodman acetic acid method as used by Leach and Lythgoe was preferred.

Other methods that have been useful in the detection of added water to milk are dependent on the preparation of the milk serum and the using of this serum in various ways such as the determination of the specific gravity, the nitrate reaction with diphenylamine, the determination of the freezing point, the determination of the electrical conductivity and the determination of the index of oxidation.

Using the specific gravity method of examination, Bull⁸ found that in eight cases 5 per cent added water was distinguishable, in ten cases 10 per cent added water was distinguishable and in fourteen cases (all examined) 15 per cent added water was distinguishable. Although the method seemed more delicate than the refractometer method, the author felt the refraction method more reliable.⁹

Varying interpretations are given to the estimation of nitrates in milk as indicating the addition of water. They are mentioned here to complete the bibliography. Tillman¹⁰ claimed that water containing 10 mg. N₂O₅ per liter could be detected when added to milk in amounts equal to 5 per cent of the milk. Galvagno¹¹ claimed that the nitrate reaction was valueless, while

¹ Reference to Villiers and Bertault, *THIS JOURNAL*, **1**, 38.

² Villiers and Bertault, *Bull. Soc. Chim.*, **19**, 305.

³ Matthes and Müller, *Z. oeffentl. Chem.*, **10**, 173.

⁴ Leach and Lythgoe, *J. Am. Chem. Soc.*, **26**, 1195.

⁵ Baier and Neumann, *Z. Nahr. Genussm.*, **13**, 369.

⁶ Ackermann, *Ibid.*, **4**, 186; *Chem. Abstr.*, **1**, 1588.

⁷ Lythgoe and Nurenberg, *THIS JOURNAL*, **1**, 38.

⁸ Bull, *Ibid.*, **3**, 44.

⁹ Woodman, *J. Am. Chem. Soc.*, **21**, 503.

¹⁰ Tillman, *J. Soc. Chem. Ind.*, **30**, 44.

¹¹ Galvagno, *Chem. Abstr.*, **3**, 2838.

¹ Leach, Textbook, "Food Analysis," 2nd Ed., p. 127.