TABLE III.

Expt.	First extract. Cc.	Washings. Cc.	At 0° $NaClO_4$ taken. G.	$KClO_4$ taken. G.	$KClO_4$ found. G.	Error. G.
1.....	A 20 + 5 + 5	W 90	0.0	0.3013	0.3011	—0.0002
2.....	A 20 + 5 + 5	W 90	0.0	0.3451	0.3449	—0.0002
3.....	A 20 + 5 + 5	W 75	0.5	0.3021	0.3027	+0.0006
4.....	A 20 + 5 + 5	W 75	0.5	0.3446	0.3450	+0.0004
5.....	A 20 + 5 + 5	W 75	0.1	0.3002	0.3005	+0.0003
6.....	A 20 + 5 + 5	W 75	0.1	0.3326	0.3329	+0.0003
7.....	A 20 + 5 + 5	W 75	0.3	0.2999	0.3002	+0.0003
8.....	A 20 + 5 + 5	W 75	1.0	0.3029	0.3033	+0.0004
9.....	A 20 + 5 + 5	W 75	1.0	0.3164	0.3168	+0.0004
10.....	A 20 + 5 + 5	W 90	0.5	0.3018	0.3019	+0.0001
11.....	A 20 + 5 + 5	W 90	0.5	0.3183	0.3183	+0.0000
12.....	A 20 + 5 + 5	W 90	1.0	0.3002	0.3004	+0.0002
13.....	A 20 + 5 + 5	W 90	1.0	0.3188	0.3189	+0.0001

TABLE IV.

			At 20°.			
14.....	A 20 + 5 + 5	W 75	0.5	0.3003	0.3007	+0.0004
15.....	A 20 + 5 + 5	W 75	0.5	0.3083	0.3084	+0.0001
16.....	A 20 + 5 + 5	W 75	0.1	0.2984	0.2983	—0.0001
17.....	A 20 + 5 + 5	W 75	0.1	0.3052	0.3053	+0.0001
18.....	A 20 + 5 + 5	W 75	1.0	0.3008	0.3010	+0.0002
19.....	A 20 + 5 + 5	W 80	1.0	0.3056	0.3059	+0.0003
20.....	A 20 + 5 + 5	W 95	0.5	0.3017	0.3019	+0.0002
21.....	A 20 + 5 + 5	W 100	0.5	0.3091	0.3093	+0.0002
22.....	A 20 + 5 + 5	W 100	1.0	0.3020	0.3022	+0.0002
23.....	A 20 + 5 + 5	W 100	1.0	0.3096	0.3099	+0.0003

It also is evident that in the procedure described the temperature is unimportant, if the washing liquid employed after the initial extraction is previously saturated with the precipitate.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

GELATIN AS AN EMULSIFYING AGENT.

BY HARRY N. HOLMES AND WM. C. CHILD.

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Various theories of the action of emulsifying agents have been offered. Plateau[1] and Quincke[2] considered the lowering of surface tension of one of the 2 liquids as the most important factor, with viscosity next. Pickering[3] believed that a droplet covering of small insoluble solid particles was a vital factor. He demonstrated his theory by the use of basic ferrous and cupric sulfates. Martin Fischer[4] states that solvated sub-

[1] Plateau, *Ann. Physik.*, **141**, 44 (1870).

[2] Quincke, *ibid.*, **271**, 580 (1888).

[3] Pickering, *J. Chem. Soc.*, **91**, 2001 (1907).

[4] Fischer, *Science*, **43**, 468 (1916); "Fats and Fatty Degeneration," Wiley and Sons (1917).

stances are the best emulsifying agents. Bancroft[1] thinks that each droplet must be covered with an adsorption layer of colloid particles in the form of a coherent film.

The object of this research was to use gelatin as a typical hydrated colloid in aiding the emulsification of oil in water and to observe the order of importance of the factors mentioned above. With kerosene-water emulsions we made a study of 2 factors usually considered as influencing stability of emulsions. (1) A study of the surface tension of the gel-oil interface; (2) a determination of whether or not gelatin is adsorbed to form a concentration layer around the oil droplets; (3) a study of the viscosity of the gelatin solutions used.

Experimental Methods.

After trying several of the best available gelatins, such as ossein stock and calf stock direct from a manufacturer, Nelson's photographic gelatins and others, we selected "Difco"[2] as the best brand for our purpose. It had an ash content of 1.1% and a water content of 13.6%. A 1.1% solution in water was so stiff that it would not flow from a 35 mm. tube when inverted. We might have lowered the ash content still further by repeated precipitation in alcohol and washing with water.

The emulsions studied were made up as follows. The gelatin was weighed into an emulsion bottle (125 cc. bottles, 35 mm. in diameter) and 10 cc. of water or the solution of some electrolyte added from a pipet. The bottle was then placed in a water-bath at 45-50° and kept there until all the gelatin was in solution, or peptized. Kerosene was then added in 5 cc. portions and the bottle placed in a shaking machine and given 1232 double strokes after each addition. The machine handled 9 bottles at a time, giving them about 4.5 complete 10-cm. strokes per second. An automatic shut-off was used to stop the shaking on the 1232nd stroke. After the last addition of oil, 3693 shakes were given the emulsion. Unless otherwise stated, all the emulsions contained 30 cc., or 75% of oil.

The emulsions were all of the oil-in-water type. They were allowed to stand for about 3 months and their conditions noted at the end of that time. Unlike soap emulsions, most gelatin emulsions are slow to cream, that is, to separate a rich emulsion layer above a very dilute emulsion layer. Those that cream first are, as a general rule, the first to show a general breakdown. We, therefore, considered the poor emulsions the ones, that creamed the fastest and separated the most oil. It was not often that the emulsion separated a uniform layer of oil on top but instead showed a general breakdown all the way through. Eight or nine bottles were grouped in a series and shaken at the same time.

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[1] Bancroft, *J. Phys. Chem.*, 17, 501 (1913).

[2] Digestive Ferments Co., Detroit.

Experimental Results.

Since the alkaline iodides and thiocyanates have a liquefying action on gelatin in water, it was assumed that this might be due to peptization, a subdivision of the particles. With smaller particles of gelatin colloidally dispersed, it seemed possible that a more coherent layer could form around the oil droplets and thus lend confirmation to Bancroft's theory.

Accordingly, 8 different concentrations of gelatin were made, varying from 0.3 g. to 1.0 g. per 100 cc. of solution, and these were all made 0.5 *M* with sodium iodide, sodium chloride and sodium nitrate as liquefying salts and 0.5 *M* with the tartrate, citrate and sulfate of sodium as solidifying salts.

It was found that with the liquefying salts more than 0.8 g. of gelatin per 100 cc. did not serve as well in stabilizing the emulsions as did lower concentrations. But with solidifying salts, which of course increase the viscosity of the liquid, the greatest permissible concentration of the gelatin was much lower, not above 0.6 g. per 100 cc. This seemed to point towards a favorable viscosity, no matter how secured, as important.

In Table I, the most generally suitable concentration of gelatin, 0.75 g. per 100 cc., was used, and the influence of liquefying salts, solidifying salts, acids and bases studied in concentrations ranging from *M*/256 to molar.

TABLE I.

Condition of emulsion in three or four months.

Gelatin per 100 cc. solution. G.	Electrolyte.	Moles of electrolyte per liter.					
		None.	1/256. 1/128.	1/64. 1/32.	1/16. 1/8.	1/4. 1/2.	1.
0.40	NaI	good	good	good	fair	fair	poor
0.75	NaI	good	good	good	fine	good	poor
1.00	NaI	fair	fair	fair	fair	fair	fair
0.40	Na_2SO_4	good	good	good	fine	good	fair
0.75	Na_2SO_4	good	good	fair	fair	poor	bad
1.00	Na_2SO_4	fair	fair	fair	poor	bad	bad
0.75	NaI	good	good	good	fine	good	poor
0.75	NaBr	good	good	good	fine	good	poor
0.75	NaCl	good	good	good	fine	good	poor
0.75	$NaNO_3$	good	good	good	fine	good	poor
0.75	NaCNS	good	good	good	fine	good	poor
0.75	Na_2SO_4	good	good	fair	fair	poor	bad
0.75	Na acetate	good	good	good	fair	fair	poor
0.75	Na tartrate	good	good	fair	fair	poor	bad
0.75	Na citrate	good	good	fair	fair	poor	bad
0.75	HCl	good	good	good	poor	bad	none
0.75	HNO_3	good	good	good	poor	bad	none
0.75	H acetate	good	good	good	good	fair	fair
0.75	Cl_3CCOOH	good	good	good	poor	bad	none
0.75	NaOH	good	good	good	fair	bad	none
0.75	LiOH	good	good	good	fair	bad	none

This table makes plain the fact that liquefying salts in 0.5 M concentration permit the formation of good emulsions with gelatin as the agent but solidifying salts in the same concentrations cause the formation of poor emulsions. An excess of any acid and especially strong acids and bases makes the emulsions very poor.

Surface Tension.—To study the surface tension at the gel-oil interface, the cold gels, made up as for emulsions, but allowed to cool without the addition of oil, were put into the shaking machine and shaken for about 5 minutes, which was enough to break completely the structure of the gels and make them about as mobile as water. The gel was then poured into a test-tube and drop numbers taken by passing oil through the gel from a Donnan pipet. The drop numbers obtained are found in Table II. Since duplicate drop numbers sometimes varied as much as 2, we made no attempt to carry our density determinations or the surface tension calculations beyond 2 figures.

Harkins[1] determines surface tension by means of the formula

$$T = (M - m)g/2\pi r f(r/V^{1/3}),$$

where m is the weight of a drop of oil, M is the weight of an equal volume of the water phase, g is the gravitational factor, 4 is the radius of the pipet tip, $f(r/V^{1/3})$ is a small function of the radius of the tip with the cube root of the volume of the drop. With the same tip used throughout we can, for comparison, reduce the equation to

$$T = \frac{k\ (\text{density water phase}) - (\text{density oil})}{\text{drop number}}.$$

This introduces an error less than 0.5% between our extreme values. This is much less than our experimental errors, and so is the formula adopted in calculating relative surface tensions for gels made up with half molar salts.

Under no conditions does gelatin compare with soap in ability to lower the surface tension of water.

When an electrolyte was present no change in surface tension was observed unless the concentration of electrolyte was at least eighth molar.

Acids, bases and liquefying salts slightly lowered surface tension at the gel-oil interface while solidifying salts raised it slightly.

As we increased gelatin from 0 g. to one g. per 100 cc. of water, the surface tension rapidly fell until the 0.30 g. content was reached and then remained constant from 0.30 g. to 1.0 g. On the other hand, a series of oil-water emulsions containing respectively, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 g. of gelatin per 100 cc. of water increased in stability rapidly up to the 0.3 g. content, but at 0.6 g. or 0.7 g. began to fall off again.

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[1] Harkins, THIS JOURNAL, 41, 520 (1919).

TABLE II.

Gelatin per 100 cc. G.	Electrolyte.	Drop number of half molar solution.	Density.	Relative surface tension.
None	Water	20 (for pure water)	1.00	100
0.75	Water	27	1.00	73
0.40	NaI	35	1.06	74
0.75	NaI	39	1.06	67
1.00	NaI	40	1.06	65
0.40	Na_2SO_4	35	1.06	74
0.75	Na_2SO_4	32	1.06	81
0.75	NaI	39	1.06	67
0.75	$NaNO_3$	34	1.03	68
0.75	NaCl	31	1.02	71
0.75	NaCNS	34	1.02	65
0.75	Na_2SO_4	32	1.06	81
0.75	NaAc	28	1.03	82
0.75	NaTart	32	1.06	81
0.75	HNO_3	34	1.02	65
0.75	HAc	32	1.01	66
0.75	NaOH	35	1.03	64

We must conclude from these results that the ability of gelatin to lower the surface tension of water from a relative 100 to 73 is not a negligible factor in emulsification.

Adsorption Films.—We found no evidence that as the oil content increased the gelatin content also had to be increased to secure an equally good emulsion. Pickering, on the other hand, found that increasing proportions of oil demanded increasing proportions of soap. In our work it appears that a definite gelatin content can be selected that makes the best emulsion for any oil content.

Thus 10 cc. of a 0.6 g. gelatin per 100 cc. $M/2$ sodium iodide gave us fine emulsions with 20, 30, 40, 60, and even 90 cc. of oil. The last emulsion was 90% of oil, very rich. The use of 0.8 g. of gelatin per 100 cc. resulted in poorer emulsions for all oil mixtures and emulsions using 1.2 g. gelatin per 100 cc. were worse yet.

Had there been any concentration by adsorption around the oil droplets the liquid below the cream should have been poorer in gelatin than the original solution. To test this we withdrew 5 cc. from the lower layer and analyzed for nitrogen by the Kjeldahl method. Even with the most dilute gelatins analysis showed a loss of only 0.0008 g., which meant nothing, since in making emulsions we did not attempt accuracy beyond one part in a thousand.

Viscosity.—We had some difficulty in measuring the viscosity of gelatin-water. It was impossible to draw up the gels in a pipet and measure time of outflow with accuracy for the structure of the gel was so altered in drawing it up that successive determinations varied by 100%. The following was the method finally adopted. Although not extremely accurate, it served very well for comparative results.

We made up the gel as for the emulsion but placed in in the shaking machine without the addition of oil and gave it 30 minutes shaking. This shaking was necessary as without it the gel was not homogeneous on cooling, and gave discordant results or at times clogged the pipets. The gels were then placed in a thermostat at 21.5° ± 0.02° and kept there for 28 hours. The tip of a short pipet was then carefully lowered into the gel and the time it took to fill the pipet under a suction of 245 mm. of water was measured by means of a stop-watch. The pipet was of 5 cc. capacity with the stem cut off short and the tip drawn down to a 0.35 mm. opening.

TABLE III.

Effect of Electrolytes on the Viscosity of Gelatin.

Molar strength.

Gelatin per 100 cc. G.	Electrolyte.	Seconds, time of flow into pipet.									
		None.	1/256.	1/128.	1/64.	1/32.	1/10.	1/8.	1/4.	1/2.	1.
0.00	$\mathrm{H_2O}$	19.5	.....	....	.....	..	.....	.....	.....	......	.....
0.40	NaI	19.0	19.6	19.2	19.6	19.4	19.2	19.5	.....	20.0	20.9
0.75	NaI	68.1	.....	74.0	68.9	54.4	33.5	20.2	.....	20.2	21.4
1.00	NaI	1039.0	912.4	695.7	640.9	385.1	108.4	23.6	.....	20.3	21.4
0.40	$\mathrm{Na_2SO_4}$	20.3	19.9	19.4	19.5	19.7	19.6	20.2	.....	21.8	21.0
0.75	$\mathrm{Na_2SO_4}$	66.3	69.2	82.9	82.8	87.4	90.4	126.8	.....	312.2	20.9
1.00	$\mathrm{Na_2SO_4}$	1000.0	(approx.)								20.8
0.75	NaCl	60.1	55.0	81.2	76.6	81.8	65.0	51.3	.....	26.8	20.2
0.75	$\mathrm{NaNO_3}$	75.8	84.3	75.7	70.8	64.8	48.6	30.8	.....	19.6	20.0
0.75	NaCNS	......	79.8	76.9	63.1	52.6	29.6	20.0	.....	19.4	19.8
0.75	NaAc	77.3	71.6	76.7	85.8	89.4	91.9	.....	180.5	297.0	527.0
0.75	NaTart	58.1	69.8	....	90.2	91.9	104.9	.....	335.0	1042.3	21.5
0.75	NaCit	......	47.8	52.9	61.1	71.1	88.4	124.7	.....	692.3	32.9
0.75	HCl	57.2	19.6	19.7	19.2	19.5	19.4	19.5	.....	19.3	19.3
0.75	$\mathrm{HNO_3}$	......	19.6	19.7	19.2	19.5	19.4	19.5	.....	19.3	19.3
0.75	HAc	79.2	45.0	22.0	19.6	19.4	19.5	19.6	.....	20.0	19.6
0.75	$\mathrm{Cl_3CCOOH}$	......	19.5	19.5	....	.....	.....	.....	.....	......	.....
0.75	NaOH	......	21.3	19.0	19.4	19.3	19.1	19.0	.....	19.4	19.7
0.75	LiOH	72.0	19.5	....	....	.....	.....	.....	.....	......	.....

Sodium tartrate, citrate, and sulfate in molar concentration precipitate the gelatin, leaving a liquid as fluid as water. Pure water ran into the pipet in 19.5 seconds and molar sodium iodide (no gelatin) ran through in about one second more. Half molar liquefiers or strong acids of any concentration reduce the viscosity of the gelatin solution nearly to that of water.

Although the viscosity measurements are rather rough, still it is noticeable that all salts when present in less than $M/32$ concentration tend to stiffen the gelatin slightly. Loeb[1] calls attention to the fact that if only

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[1] Loeb. *J. Biol. Chem.*, 33, 531 (1918).

dilute salts are used or if the excess is washed out, sodium chloride, bromide, iodide, nitrate, sulfate, acetate, tartrate and citrate all increase the swelling of his gelatin. That is, if the excess of salt is washed out, the salts do not follow the Hofmeister order which rules that the first salts mentioned cause more swelling than pure water and that the latter cause less, but they all have the same effect. Where we are using 0.75 g. of gelatin per 100 cc. we also notice that all salts when dilute have a similar effect. However this stiffening produced by the dilute liquefying salts is very slight.

By comparing Tables I and II and III with the other data, we see that the ability of gelatin to make a good emulsion can be summed up in the statement that provided that at least 0.3 g. of gelatin per 100 cc. of solution is used, any gel of less than 40 seconds flow will make an excellent emulsion, any gel of less than 100 seconds flow will make a good emulsion. The farther above this value we go the poorer the emulsion. On the other hand, we cannot use strong acids above *M*/16 or strong bases above *M*/8, or salts above 0.75 *M*. In other words, the liquefying must not be carried too far. Whether the gel is made too stiff by an excess of gelatin or by the presence of much solidifying salt the emulsion is much poorer. Since this is true no matter how surface tension varies we believe that viscosity plays the dominant part in the stability of gelatin emulsions.

All these stability tests required long standing. For a final test we added oil in small portions, shaking intermittently until another addition of oil broke the emulsion. Table IV gives the results.

TABLE IV.
Order of Breaking of Emulsions on Overloading with Oil.
Grams of Gelatin Per 100 cc. of Solution.

	0.1.	0.2 and 0.3.	0.4, 0.6 and 0.8.	1.2.	1.6.	2.4.
NaI	1st	2nd	3d	4th	5th	last
H_2O	1st	2nd	3d	last	2d	1st
Na_2SO_4	1st	2nd	last	3d	2d	1st

When a gel was highly liquefied by sodium iodide the most concentrated gelatin, 2.4 g. per 100 cc., was the last to break, that is, we were able to add more oil to it than to any other before breaking. With no salt present the same gelatin content of 2.4 g. per 100 cc. was one of the first of the whole series to break. In the absence of any salt a gelatin content of 1.2 g. per 100 cc. was loaded with oil as heavily as any. With sodium sulfate the higher gelatin content took up the least oil before breaking. It is to be noted that the solutions withstanding the greatest overloading with oil are not those giving the stablest emulsions as measured by long standing. It is clear that too great viscosity is just as prejudicial to emulsion stability as too little. The viscosity and hydration of gelatin are closely related. Salts and acids compete with gelatin for the water present but they also peptize gelatin. It must be that both degree of hydration and size of peptized particles are important only insofar as they secure favorable viscosity.

Summary.

When kerosene was emulsified in water by the aid of gelatin it was found that:

1. The maximum lowering of surface tension should be secured. This is obtained just as well by 0.3 g. or 0.4 g. of gelatin per 100 cc. of water as by 1.0 g. Acids, bases and liquefying salts also lower it a little while solidifying salts raise it.

2. Viscosity must not be increased more than a little beyond that of water. This means either (1) that only a small amount of gelatin can be used or (2) that the gelatin must be liquefied by the proper electrolytes. The latter method yields the better emulsion.

3. An excess of acid, base or liquefying salt should not be used. This probably means that the structure of the gelatin must not be entirely destroyed or that it must not be reduced to near molecular sizes.

4. There is no convincing evidence that gelatin particles are withdrawn from the solution to form adhesion layers about the oil droplets.

5. There is no evidence that as the oil content is increased the gelatin content must also be increased in order to produce as good an emulsion. This would surely be the case were adhesion layers formed around the oil droplets. One gelatin content in a given volume of water can be selected that will make the best emulsion for all oil contents.

6. The leading factor in oil-water emulsification with the aid of gelatin is viscosity, not the maximum but the most favorable viscosity. These conclusions refer only to gelatin, but investigation may show that they apply to all highly hydrated compounds.

OBERLIN, OHIO.

NOTE.

The Separation of Iron from Aluminum by Precipitation as Prussian Blue.—In Dr. Ddgar F. Smith's "Chemistry in Old Philadelphia," it was suggested[1] that a study should be made of the possibility of a quantitative separation of iron from aluminum by precipitation as prussian blue. The work of Robinson[2] showed that double and triple ferrocyanides of magnesium, aluminum and cerium are formed when solutions of the chlorides of these metals are mixed with potassium ferrocyanide. He tried only 0.5, 0.25 and 0.125 *N* solutions.

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[1] P. 47.

[2] Robinson, *J. Chem. Soc.*, **95**, 1356 (1909).