

## SUSPENSIONS IN DILUTE ALKALINE SOLUTIONS.

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The purpose of this article is to publish an uncompleted experiment. The lapse of several years has made it seem probable that we will not be able to complete it. The phenomena described are well worth study and explanation or co-ordination.

In connection with the regularities or laws which have been discovered in the coagulation of colloidal solutions or the precipitation and sedimentation of suspensions, it had been early found that the coagulating power of an ion was not only dependent upon its kind and valence but also upon its rate of migration. There seemed to be still other causes of irregularity which may be better understood when the peculiarities described in the following notes are explained.

The experiments here described were made by Mr. Alonzo Straw in the winter of 1903 at the Massachusetts Institute of Technology.

It is Bredig who first observed that colloidal gold and colloidal platinum solutions as prepared by the sub-aqueous arc method are made much more stable by the addition of a trace of alkali—either sodium or potassium hydroxide. He found, for example, that the addition of sufficient sodium hydroxide to make the colloidal gold solution 0.001 N remarkably increased the stability of the solution. He furthermore says that the action of alkalis in the coagulation of colloidal solutions is effective, for the moderately diluted alkalis coagulate the colloids as energetically as dilute acids. Later, in his article written with R. Muller v. Berneck<sup>1</sup>, he shows that the speed of the catalytic action of colloidal platinum is increased by the addition of a little alkali. The fact also corresponds with Jacobson's observation that a little alkali increased the catalysing power of organic ferments, while with more or less than a definite concentration, the power was reduced.

Facts like these lead to the belief that a dilute alkaline solution of a definite concentration, which may not in all cases be the same, has certain peculiar effects. This effect may be due to a change in the surface tension of the solution, or it may be due, as Bredig assumes, to an increase in the OH ions to a certain concentration, after which there is a decrease in the stability of colloids, due to the excess of OH ions. Whatever the explanation, the fact is proven that dilute solutions of alkali hydroxides possess peculiar properties in their relationship to the colloidal state.

The purpose of this paper is to show that suspensions of several kinds are peculiarly affected as regards their stability by the presence of alkali.

It was noticed when emulsions were made by shaking with water such substances as turpentine, carvene, and the like, that, although they clar-

<sup>1</sup> R. Muller v. Berneck & Bredig—Z. Phys. Chem. 31, 296.

ified quickly on the addition of salts or acids, as is the case with all colloidal suspensions; yet when a small quantity of sodium hydroxide was added, the emulsions did not clarify nearly so quickly. In many cases they did not clarify for a long time. On the other hand, when a large quantity of sodium hydroxide was added, the emulsions clarified quickly.

We wished to find a few substances affected in the way described and also to determine if possible, whether the emulsions and suspensions were most stable at some definite concentration of alkali.

About the same procedure was followed in each of the following cases. Emulsions of turpentine and water, carvene and water, and carvol and water were first used. A definite volume of the organic substances was measured in a pipette, and was run into each of a series of 5-inch test-tubes. The tubes were as nearly as possible of the same inside diameter, so that when all were filled to the same height, the volume in each would be about the same. To the first tube in the series about 10 cc. of water were added and no alkali, to the second tube a smaller volume of water, a known volume of an  $N/8$  sodium hydroxide solution and then the tube was filled to the height of the water in the first tube. Only the very slightest trace of alkali was added to the second tube. To the third a little more was added, and so on, the amount of alkali being increased in each successive tube. In every case we diluted as above to the same final volume with distilled water. The tubes were then tightly corked and all shaken violently at the same time. They were then allowed to stand until the emulsion was partially clarified. They were then photographed. Those tubes were selected which best showed the stages of clarification. The first tube to which no alkali had been added was also photographed.

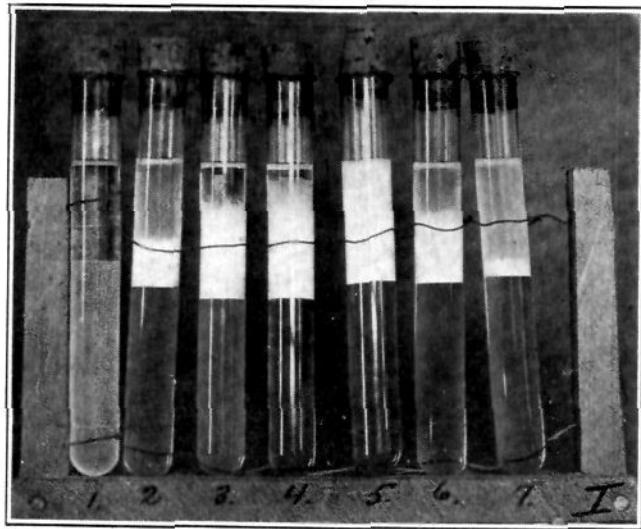
After photographing, 5 cc. of the clear solution at the bottom of each tube were titrated against an  $N/5$  nitric acid solution, using phenolphthalein as an indicator, and an  $N/200$  solution of potassium hydroxide to titrate to a neutral point.

I. *Turpentine Emulsion*.—An emulsion of turpentine with water and dilute alkali was made as above described, using 5 cc. of turpentine and making up the final volume to about 15 cc. in each tube. For titration 5.00 cc. from a calibrated pipette were used. The photograph was made about two days after emulsification.

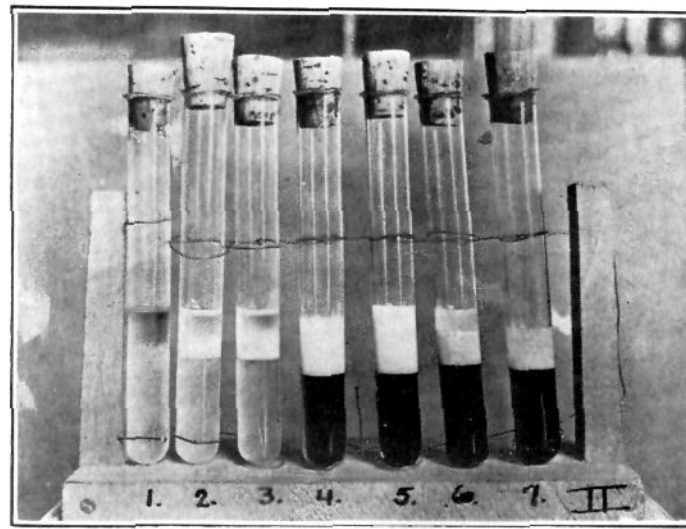
Below are the concentrations of the solution. The photograph shows a varying state of emulsification or suspension of the water in the turpentine. This stability finds its maximum when the concentration of the alkali in the water is about 0.008 N.

- |                              |                             |
|------------------------------|-----------------------------|
| 1. 0.003 N Acid (nitric)     | 4. 0.003 N Sodium hydroxide |
| 2. 0.0003 N Sodium hydroxide | 5. 0.008 N " "              |
| 3. 0.002 N " "               | 6. 0.012 N " "              |
| 7. 0.02 N Sodium hydrate     |                             |

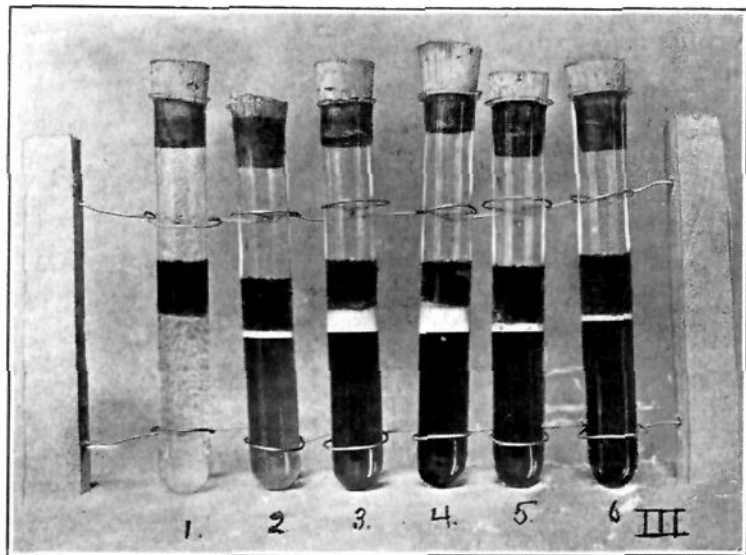




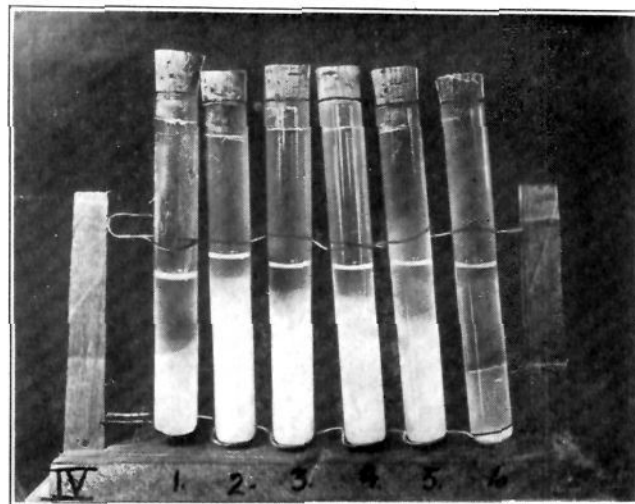
I. Turpentine.



II. Carvene.



III. Carvol.



IV. China Clay.

The figures should be regarded more as relative than actual true values, although they are not very far from the true values.

II. *Carvene Emulsion*.—Similar emulsions were made by shaking carvene with water and with dilute alkali. 2 cc. of carvene were used instead of 5 cc., as in the previous case. The first two tubes being acid, it was not thought necessary to titrate them. These were allowed to settle ten days after emulsification before being photographed. Here then is also a point of maximum stability which corresponds to about 0.0002 N.

1. Acid (not titrated)	4. 0.0001 N Sodium hydroxide
2. " " "	5. 0.0002 N " "
3. 0.00005 N. Sodium hydroxide	6. 0.0004 N " "
7. 0.001 N Sod. hydroxide	

In the case, for example, of No. 3 the solution was sufficiently alkaline to give a red coloration to phenolphthalein and the slightest trace of acid neutralized it. While from the analysis this was the result obtained, in reality, this value can have little actual significance. Taking the whole series, the figures for the normality are approximately and relatively correct.

III. *Carvol-water Emulsion*.—An emulsion was made as above, using carvol instead of carvene or turpentine. 2 cc. of carvol were used, and the tubes were allowed to stand two days after emulsification before photographing. The clear solution was titrated as usual. Below are the results of this titration.

1. 0.002 N Acid	4. 0.002 N Sodium hydroxide
2. 0.001 N "	5. 0.0025 N " "
3. Neutral or trace alkali	6. 0.004 N " "

Other emulsions, like those of terebene, safrol and a terpeneole showed that a trace of alkali preserved the frothiness for a longer time, but the effect was not sufficiently marked for photographing.

In a similar manner ordinary suspensions like china clay in water and lamp black in water were tried. In each of these cases a considerable quantity of the substance was shaken with water and from this mixture portions of 5 cc. were taken, being careful to shake the mixture before taking each portion. The alkali solution was added to each tube as before and all made up to the same volume with water. The tubes were then allowed to stand and when sufficiently clarified, they were photographed. 5 cc. of the clear solution filtered from the mass in the tube were titrated with acid as before.

IV. *China Clay*.—Suspensions in tubes were made as above with china clay and dilute sodium hydroxide solutions. These had been allowed to stand two days after shaking before photographing.

Below the photographs are given the concentration obtained by titration. In this case the concentration of greatest stability is not so clearly

marked as in other cases, but there can be no doubt even here as to its existence.

- |                             |                               |
|-----------------------------|-------------------------------|
| 1. Neutral                  | 4. 0.00075 N sodium hydroxide |
| 2. .0004 N sodium hydroxide | 5. 0.0018 N " "               |
| 3. .0005 N " "              | 6. 0.0034 N " "               |

#### Lamp Black.

V. Suspensions of lamp black were prepared as described above. They were allowed to stand one day after shaking before photographing. They show the same increase of stability as other suspensions with a maximum at a concentration not far from 0.001 N.

- |                              |                             |
|------------------------------|-----------------------------|
| 1. Neutral                   | 4. 0.001 N sodium hydroxide |
| 2. 0.0004 N sodium hydroxide | 5. 0.002 N " "              |
| 3. 0.0006 N " "              | 6. 0.004 N " "              |
| 7. 0.006 N sodium hydroxide. |                             |

#### Colloidal silver with dilute sodium hydroxide.

VI. As a matter of interest the following photograph is inserted to show the effect of alkali on colloidal silver, though the data are meager.

Tubes of this colloid with water and dilute sodium hydroxide solution were prepared in much the same manner as those previously described. To each of a series of tubes containing 5 cc. of the colloid solution and a trace of  $N\frac{1}{8}$  sodium hydroxide solution were added, increasing the amount of alkali in each successive tube. These tubes were then all filled to the same height with water, making the volumes the same. The tube containing no alkali at all is unfortunately not shown in the photograph. In this tube the colloid was as stable as in tube No. 2 and it could only be ascertained in which of these two the colloid was more stable, by allowing them to stand a long time, perhaps months. The tubes shown were allowed to stand about 18 hours after shaking before being photographed.

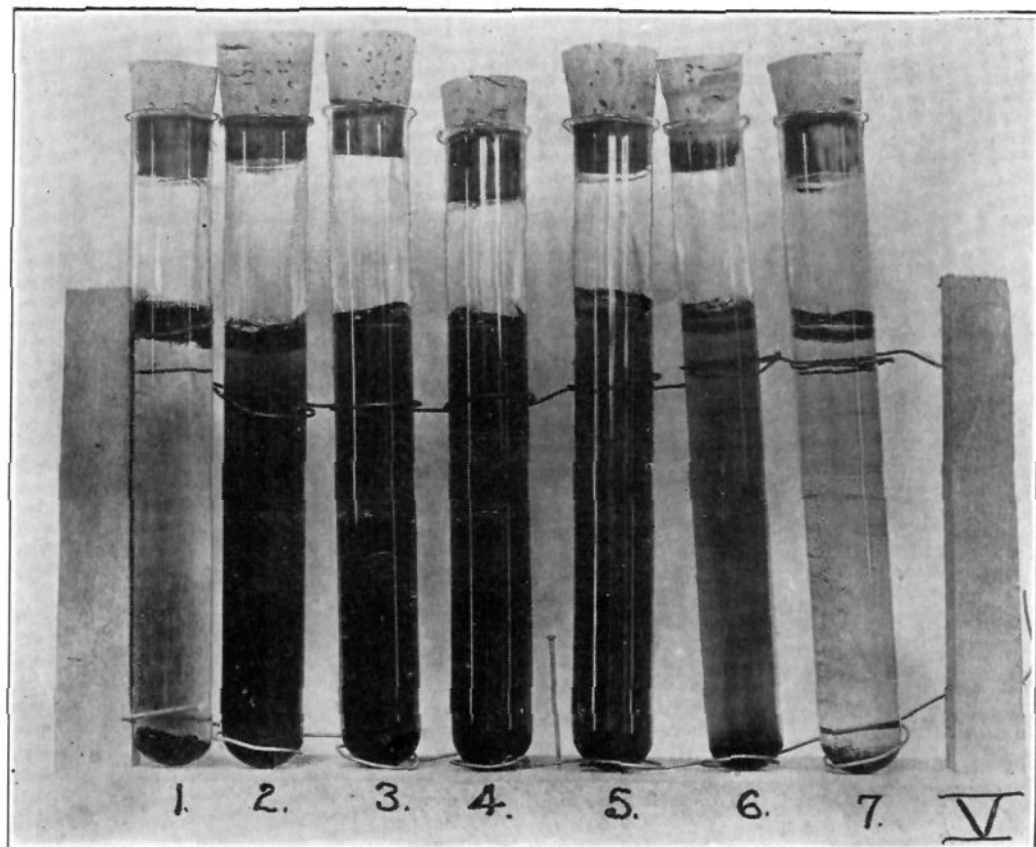
- |                             |
|-----------------------------|
| 1. 0.002 N Sodium hydroxide |
| 2. 0.004 N " "              |
| 3. 0.011 N " "              |

#### Conclusion.

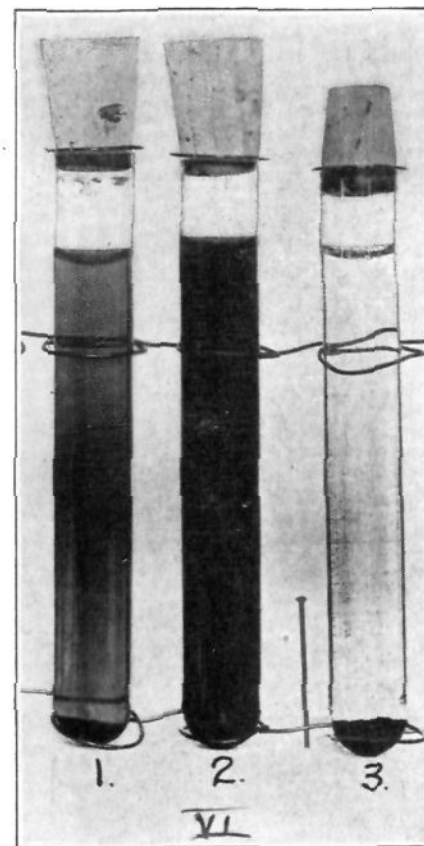
The photographs show very plainly to the eye that, not only does the presence of a trace of alkali increase the stability of colloids, as Bredig observed, but also has the same effect in increasing the stability of emulsions and suspensions.

The effect is probably due to an increase in the surface-tension of the solution. But so far as can be ascertained, no work on the surface-tension of such dilute sodium hydroxide solutions has been recorded and therefore, the effect cannot be positively ascribed to that cause.

The methods employed for the determination of the concentrations of



V. Lamp black.



VI. Silver.





the solutions were not, it must be confessed, sufficiently delicate for so dilute solutions. Yet as has been stated, they will at least show the relative strength of the solutions.

The conclusions that we have here a case of small changes in surface tension of the liquid which changes also change in sign in the case of alkali at very feeble concentration, seemed at first not to be in accord with measurements of other properties of such solutions, nor were there indications of such co-ordinations in the published work on surface tension so far as we know. One exception was found, however, and this adds interest to these experiments. Bliss describes experiments by which he studied the forces between particles in liquids. In these experiments he observed the changes in the Newton rings, produced by very light pieces of flat microscope-specimen cover-glasses which were supported on the convex surface of a large lens under water. These Newton rings served to measure the distance between the flat and the convex glass surfaces, in terms of wave-lengths of light. He noted that when caustic potash solution was added to the water covering the glass surfaces, very marked changes were produced in these rings and he writes "A trace of KOH less than 0.0007 gm. per cc. increases the layer between the glass surfaces, excess beyond this trace causes it to fall back again."

It is very probable that the effect noted by Bliss is intimately connected with the above described phenomena of increased stability of colloids, due to traces of alkali. Our own experiments as well as those described by Bliss, were not carried out with a high degree of quantitative accuracy. It is not impossible that the alkali concentration corresponding to maximum stability for different suspensions or colloids is really the same in each case and that the differences which our analyses show are due to error of some sort. For this reason and in the hope that some one will be tempted to carry on this work it was thought worth while to publish this paper.

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## FURTHER STUDIES OF SUPERCOOLED LIQUIDS.

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In a number of previous papers<sup>2</sup> it has been pointed out that crystallization and solidification from a supercooled liquid is very considerably influenced by the previous treatment to which the liquid has been subjected, especially by the temperature to which it has been heated and the length of time which it has been maintained at a given temperature. All the results heretofore published have been based upon observations on the

<sup>1</sup> Phys. Rev. 1895, 241, 273.

<sup>2</sup> Young and Burke, This Journal, 28, 315, and references there cited.