

3d. Staphylococcus is a logical organism to use for such tests, but on account of the variation in resistance of different strains of the organism, no result can be taken as final and invariable.

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THE EFFECT OF VARIOUS IONOGENS ON THE TIME PERIOD REQUIRED FOR THE GELATION OF COLLOIDAL SILICIC ACID.*

BY LOUIS F. WERNER.

The retarding and accelerating effect of ionogens upon the setting of (sol) colloidal silicic acid has been the subject of study of quite a number of investigators in the past, but the results achieved have not always been harmonious or comparable. This was due, apparently, to the fact that the various investigators were experimenting with colloidal silicic acid of various concentrations and varying degrees of hydration.

It was endeavored therefore, in the work undertaken, to work with a pure silicic acid of uniform concentration, and of like hydration.

METHOD OF PREPARATION USED IN MAKING THE COLLOID.

The colloidal silicic acid was made by diluting 50 mls of commercial sodium silicate solution (density 40° Beaumé) with 150 mls of distilled water, and then adding this solution, with constant stirring, to 50 mls of pure concentrated hydrochloric acid. The mixture was dialyzed, using a "Parlodion" bag, made by coating the inside of a 350-ml Erlenmeyer flask with an ether alcohol solution of that substance, and separating from the flask after the solvent had vaporized.

The dialysis was carried out in a tall cylindrical glass vessel holding about 3 liters of water, and wide enough to prevent the dialyzing capsule from touching the sides. The water (distilled) was changed after 3, 3¹/₂, 15, and 6 hours. The total time of dialysis was therefore 29.5 hours, and this method was rigidly followed in each batch of colloidal silicic acid prepared. The product secured in this way was but slightly translucent, and gave but a slight opalescence with silver nitrate solution. Further dialysis to remove this slight trace of chloride always resulted in gelation.

EXPERIMENTAL METHOD.

The method of procedure was to pipette out the required amount of ionogen solution, dilute with the required amount of distilled water to make 4 mls of the mixture, and then 4 mls of colloid solution added, thoroughly mixing after each addition. The tubes were then allowed to stand until no evidence of flow was noted upon inverting the tube. This point was taken as the end-point.

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The author does not claim any great numerical accuracy for the work, as there were certain factors which prevented absolute accuracy, but the results achieved in many cases were of great significance.

As many salts suffer hydrolysis upon solution in water, giving either an alkaline or acid solution, it was thought fundamental that the effects of acids and bases be first investigated, as the results would probably throw some light upon the behavior of these salts with colloidal silicic acid.

In the following tables, the first column gives the concentration of the ionogen in the final mixture, and the remaining columns, the time in days, hours or minutes, as noted in the table. The "check" was merely the average time taken for three tubes containing 4 mils of distilled water and 4 mils of the colloid to set.

EFFECT OF VARIOUS ACIDS AT DIFFERENT CONCENTRATIONS UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Concentration (normal).	Time in days.			
	H ₂ SO ₄ .	HCl.	HNO ₃ .	CH ₃ COOH.
0.5000.....	10.0	19.0	8.0	39.6
0.4000.....	12.5	22.3	8.7	39.6
0.3000.....	14.8	30.0	9.9	39.6
0.2000.....	17.0	38.0	11.8	39.6
0.1000.....	23.0	42.0	14.0	31.6
0.0200.....	23.0	37.0	18.3	20.0
0.0100.....	20.0	21.0	16.6	17.0
0.0010.....	14.0	17.0	9.6	8.6
0.0005.....	11.5	9.6	8.8	7.6
Check		7.0		

The results show that the general effect of acids upon colloidal silicic acid is to peptyze it, but there is a difference in behavior in the case of the highly ionized and the slightly ionized acids. Thus in the case of sulphuric, nitric and hydrochloric acids, the greatest peptyzing effect is not at the highest concentration, but at a middle point. In the case of acetic acid, however, the greatest peptyzing effect of the acid was at the highest concentration of the acid.

EFFECT OF BASES OF VARIOUS CONCENTRATIONS UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Concentration (normal).	Time in days.	
	NaOH.	NH ₄ OH.
0.5000.....	30.7	x
0.4000.....	28.0	x
0.3000.....	28.0	x
0.2000.....	32.3	x
0.1000.....	68.7	x
0.0200.....	x	x
0.0100.....	x	x
0.0010.....	x	x
0.0005.....	82.0	65.0
Check	7.5	

NOTE.—(x) signifies that the contents of tube did not set after 100 days.

From the above results it is apparent that sodium hydroxide had its greatest peptyzing effect at a very slight concentration, above and below which this effect

diminishes. Little can be said of ammonium hydroxide, due to the failure of the tubes to set, but it is apparent that it has a greater peptyzing effect than sodium hydroxide.

EFFECT OF POTASSIUM CHLORIDE UPON ACID AND ALKALINE SOLUTIONS OF COLLOIDAL SILICIC ACID.

Concentration (normal) KCl.	Time in days.			
	CH ₃ COOH.	HCl.	NaOH.	NH ₄ OH.
0.5000	36.3	31.4	1.5	At once
0.3750	36.3	31.4	3.2	At once
0.2500	36.3	31.4	5.4	3 minutes
0.1250	36.3	31.4	10.5	246 minutes
0.0500	36.3	31.4	13.8	966 minutes
0.0375	36.3	31.4	17.5	x
0.0250	36.3	31.4	18.5	x
0.01250	36.3	31.4	x	x
0.0025	36.3	31.4	x	x
0.0005	36.3	31.4	x	x
Check	36.0	31.2	x	x

NOTE.—(x) signifies that the contents of tube did not set after 100 days.

In this set of experiments, the strength of the alkali or acid was of quarter normal strength in each tube, after the final mixture was made, the strength of the potassium chloride alone varying. The check consisted of 4 mils of half normal alkali or acid mixed with 4 mils of colloidal silicic acid.

The results showed that in acid solution, both of strong and weak acids, the time of setting was not affected by the addition of potassium chloride; in the case of bases, however, the time of setting was reduced, this being true for a weak and a strong base. The significance of these results is that it throws some light upon the behavior of salts which are hydrolyzed upon solution in water with colloidal silicic acid. As some of the salts used in the following experiments were of this type, these results were of great assistance in explaining the abnormal behavior of these compounds with the colloid.

EFFECT OF THE VARIOUS POTASSIUM SALTS UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Normal concentration of salt.	Time in hours.			
	KI.	KNO ₃ .	K ₂ SO ₄ .	KBr.
0.50000	6.0	5.5	5.3	5.9
0.37500	8.0	7.5	8.3	8.8
0.25000	10.0	9.0	12.3	10.2
0.12500	16.0	11.5	15.3	15.9
0.05000	20.0	15.5	24.3	29.9
0.03750	22.0	20.5	28.3	31.9
0.02500	27.0	21.5	38.3	34.9
0.01250	33.0	21.5	39.2	36.9
0.00500	40.1	24.3	46.2	51.8
0.00375	45.2	28.3	48.3	54.8
0.00250	49.1	63.3	64.6	59.0
0.00125	49.1	87.3	73.3	70.9
0.00063	62.7	94.3	80.5	70.9
0.00025	76.0	112.3	89.3	82.8
Check	172.0			

The results show that the effect of the potassium salts is to shorten the time of gelation of the colloid, the effect being greatest at the greatest concentration.

EFFECT OF THE CHLORIDES OF THE VARIOUS METALS UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Molal concentration of salt.	Time in hours.				
	NaCl.	KCl.	NH ₄ Cl.	CaCl ₂ .	BaCl ₂ .
0.50000	4.8	3.2	2.5	1.9	3.0
0.37500	7.8	4.2	4.5	4.3	5.0
0.25000	14.8	7.2	5.9	5.9	14.0
0.12500	22.8	14.2	16.5	12.9	18.0
0.05000	23.8	18.2	21.5	16.9	38.0
0.03750	25.3	19.2	24.4	17.9	40.0
0.02500	27.3	20.3	24.5	18.8	42.0
0.01250	29.0	20.5	25.5	19.9	51.0
0.00500	40.0	22.0	27.0	20.9	52.6
0.00375	46.8	40.2	48.9	53.0	53.0
0.00250	50.8	48.9	76.0	53.0	55.0
0.00125	52.0	49.2	101.0	58.7	62.0
0.00063	54.4	43.2	110.0	58.7	62.0
0.00025	63.2	64.2	117.0	65.9	62.0

Molal concentration of salt.	Time in hours.			
	SrCl ₂ .	MgCl ₂ .	CuCl ₂ .	FeCl ₃ .
0.50000	2.9	2.3	114.3	x
0.37500	4.9	4.4	108.6	x
0.25000	7.0	7.4	85.0	x
0.12500	19.0	14.3	73.0	x
0.05000	24.0	18.3	70.0	x
0.03750	27.0	24.2	65.0	x
0.02500	32.0	24.8	65.0	x
0.01250	57.0	25.3	63.3	x
0.00500	68.0	25.8	83.0	x
0.00375	75.0	84.0	85.1	x
0.00250	79.0	86.0	97.0	1464.0
0.00125	90.0	90.3	101.0	1056.0
0.00063	91.0	114.0	107.0	384.0
0.00025	92.0	115.3	109.0	336.0
Check	192.0			

The results showed, with the exception of the ferric chloride and the cupric chloride, that the action of the chlorides of the various metals was to accelerate the setting of colloidal silicic acid. The peculiar behavior of the cupric chloride and ferric chloride was undoubtedly due to hydrolysis of these salts.

With the exception of disodium phosphate at high concentrations, the mono- and disodium phosphates behaved very much as did the ordinary neutral salts already experimented with. There was no apparent reason for the jelling effect of the disodium phosphate falling off so rapidly as the concentration decreases, except that hydrolysis of this salt would be more pronounced, and then we would have the peptyzing effect of the alkali. The strong peptyzing effect of the trisodium phosphate is readily explicable, as trisodium phosphate is readily hydrolyzed by water, giving sodium hydroxide and disodium phosphate, so that the results were analogous to those secured in the work upon sodium hydroxide.

EFFECT OF THE THREE SODIUM PHOSPHATES UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Molal concentration of salt.	Time in hours.		
	NaH ₂ PO ₄ .	Na ₂ HPO ₄ .	Na ₃ PO ₄ .
0.50000	5.5	2 minutes	x
0.37500	6.0	3 minutes	x
0.25000	6.7	6 minutes	60.0
0.12500	7.5	2.6	84.0
0.05000	8.5	3.2	432.0
0.03750	9.5	3.7	1704.0
0.02500	12.6	12.2	1956.0
0.01250	15.6	39.2	1956.0
0.00500	23.6	43.2	1860.0
0.00375	47.0	48.2	1812.0
0.00250	64.0	69.2	1716.0
0.00125	71.0	71.3	1140.0
0.00063	84.0	87.3	732.0
0.00025	95.0	95.2	106.0
Check	172.0		

EFFECT OF THE THREE SODIUM CITRATES UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Molal concentration of salt.	Time in hours.		
	Monosodium.	Disodium.	Trisodium.
0.50000	40.2	2.1	1 minute
0.37500	40.2	2.1	2 minutes
0.25000	40.2	2.7	3 minutes
0.12500	40.2	2.7	4 minutes
0.05000	40.2	3.1	9 minutes
0.03750	40.2	3.3	11 minutes
0.02500	40.2	4.0	13 minutes
0.01250	40.2	5.0	23 minutes
0.00500	40.2	7.1	1.0
0.00375	40.2	12.0	2.0
0.00250	40.2	13.0	3.0
0.00125	40.2	24.0	5.0
0.00063	40.2	29.0	11.0
0.00025	40.2	31.6	16.0
Check	156.7		

The results showed that the di- and trisodium citrates had a powerful gelation effect upon the colloid, which effect decreased with the concentration. The effect of the monosodium citrate was analogous to the condition where we have an acid in the presence of a salt, all the tubes set in the same time, as was the case upon adding KCl to acid solutions.

In the work upon the acetates of the various metals, it was found that these salts exceeded all other ionogens in their jelling effect upon the colloid. With the exception of mercuric acetate, this effect varied with the concentration, but in this case the mercuric acetate had the greatest effect at low and high concentrations. Probably this exceptional behavior is due to hydrolysis, although the salts of mercury are peculiar in themselves as compared with those of other metals.

The effect of the inorganic salts of the "heavy metals" showed the greatest jelling effect was at a medium concentration, and was least at high or low concen-

EFFECT OF THE VARIOUS ACETATES UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Molal concentration of salt.	Time in minutes.						
	Cu(Ac) ₂ .	Hg(Ac) ₂ .	Pb(Ac) ₂ .	Ba(Ac) ₂ .	Ca(Ac) ₂ .	KAc.	Mg(Ac) ₂ .
0.50000	1/30	12	9	33	11
0.37500	1/20	14	15	38	13
0.25000	1/15	15	17	38	17
0.12500	1/12	1258	5	18	21	42	22
0.05000	1/2	1468	27	26	27	48	31
0.03750	3	1678	30	32	32	53	38
0.02500	7	2548	42	38	39	63	46
0.01250	32	2668	81	54	59	152	71
0.00500	97	3328	179	104	109	158	100
0.00375	167	3808	238	139	134	249	136
0.00250	186	2808	305	145	168	293	160
0.00125	246	2548	500	174	309	413	203
0.00063	303	2008	620	300	429	563	256
0.00025	418	1888	920	405	969	893	421
Check	10010						

EFFECT OF THE SALTS OF THE "HEAVY METALS" UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Molal concentration of salts.	Time in hours.		
	HgCl ₂ .	CuCl ₂ .	Pb(NO ₃) ₂ .
0.50000	...	114.3	51.0
0.37500	...	108.6	47.1
0.25000	...	85.0	35.0
0.12500	127.3	73.0	32.0
0.05000	119.3	70.0	15.1
0.03750	112.3	65.0	16.0
0.02500	99.3	65.1	18.0
0.01250	87.3	65.0	20.1
0.00500	75.3	79.6	30.1
0.00375	63.4	85.0	34.1
0.00250	44.4	97.0	39.0
0.00125	43.4	101.0	51.1
0.00063	67.3	107.0	63.0
0.00025	79.4	109.0	75.0
Check	100.1		

trations. These results are analogous to the results obtained in the work with strong acids, and as these salts are hydrolyzed in aqueous solution, this peculiar behavior must be due to the free acid formed in this hydrolysis.

The accelerating effect of the alkali metal salts of organic acids upon the time of gelation of silicic acid was very marked, and grew greater as the concentration of the salt increased. A peculiar result was the great effect of the carbonates and bicarbonates at high concentration, and the great falling off of this effect at lower concentrations. There was no apparent reason for this phenomenon, except it was that the carbonate and bicarbonate of sodium are hydrolyzed at these lower concentrations, giving a solution of sodium hydroxide and carbon dioxide, and then we have the peptyzing effect of the sodium hydroxide, and not the effect of the carbonate and bicarbonate. The jelling effect of the neutral salts of the organic acids; citrates, acetates, carbonates, lactates and oxalates, can only be explained as being due to the carboxyl group present in each.

EFFECT OF THE ALKALI METAL SALTS OF THE ORGANIC ACIDS UPON THE TIME OF SETTING OF COLLOIDAL SILICIC ACID.

Molal concentration of salt.	Time in minutes.				
	Na ₂ CO ₃ .	NaHCO ₃ .	KNaC ₄ H ₄ O ₆ .	Li lactate.	K ₂ C ₂ O ₄ .
0.50000	7	5	9	36	9
0.37500	25	8	15	42	19
0.25000	595	35	23	44	24
0.12500	66 days	56	28	49	27
0.05000	x	x	36	72	39
0.03750	x	x	39	82	47
0.02500	x	x	55	92	59
0.01250	x	x	78	137	69
0.00500	x	x	153	257	144
0.00375	x	x	243	377	264
0.00250	x	x	454	737	384
0.00125	x	x	634	1067	564
0.00063	67 days	47 days	814	1277	744
0.00025	2.5 days	13.9 days	1354	1457	1284
Check	9403 (6.5 days)				

The results obtained with these salts and phosphates have caused some doubts to arise in the author's mind as to the correctness of the hypothesis that the setting of (sol) colloidal silicic acid is due to hydration. The organic salts mentioned above contain most of the well-known diuretics, and as these act primarily by extracting water from the tissues, and *in vitro* prevent the swelling of gelatin, and as silicic acid and gelatin are typical examples of a certain class of colloids, there are but two rational conclusions to be drawn: that these salts act directly opposite in the case of silicic acid to the observed effect upon organic colloid, *i. e.*, in the case of gelatin they dehydrate, and in the case of silicic acid they hydrate; or we must assume that the setting of colloidal silicic acid is a dehydration phenomenon.

It would be quite remarkable that this difference in behavior should be so consistently opposite throughout a whole series of salts such as these, so that the logical conclusion would seem to be that the setting of (sol) colloidal silicic acid is caused by dehydration. Synuresis, which takes place after jelling of silicic acid, would apparently support this hypothesis, although of itself it does not constitute any strong evidence.

SUMMARY.

The results of the work showed that acids had a very powerful peptyzing effect upon sol colloidal silicic acid, but in the case of the strong acids this effect was strongest at medium concentrations. Alkalies also had a strong peptyzing effect; in the case of the strong alkalies the peptyzing effect was greatest at medium to low concentrations, but in the case of the slightly ionized base, the peptyzing effect was great in all but low concentrations.

The effect of salts in the presence of both weak and strong acids was nil but hastened the setting of the colloid in the presence of both strong and weak bases.

The potassium salts of various negative radicals were all found to decrease the time required for the gelation of the colloidal silicic acid, but the time required did not differ greatly in the case of the various salts.

The chlorides of various metals, with the exception of ferric chloride and cupric chloride, were found to lessen the time required for the gelation of the colloid, although the difference in basic radical caused no great difference in this period.

The two acid sodium phosphates were found to cause silicic acid to jell very rapidly, but the trisodium phosphate at strong and medium concentrations had a strong peptyzing effect. The di- and trisodium citrates accelerated the setting of the colloid greatly, the effect decreasing with the concentration, but in the case of the monosodium citrate, the time required for the setting of the colloid was the same at all concentrations.

The acetates of various metals had the greatest jelling effect, notably the acetates of the "heavy metals," excepting mercury. The effect of the inorganic salts of the "heavy metals" was slight.

The alkali salts of the various organic acids had an extremely powerful accelerating effect upon the setting of colloidal silicic acid, although the carbonates and the bicarbonates had a peptyzing effect in medium to dilute concentrations.

CINCINNATI, OHIO.

THE DETECTION OF WOOD ALCOHOL IN BEVERAGES, ETC.*

BY JOSEPH L. MAYER.

Complying with the request of the New York City Health Commissioner, many local pharmacists are now dispensing whiskey on physicians' prescriptions, and due to the number of deaths which resulted recently from drinking beverages containing wood alcohol, many inquiries are being made for a test to detect this dangerous adulterant.

The test for the detection of methyl in ethyl alcohol, found on page 36 of the United States Pharmacopoeia (which is practically that of Denigès), is not of much value when applied to beverages, etc., as sugar and glycerin in the distillate will give a weak reaction, indicating the presence of methyl alcohol where none occurs.

The method, which was official in the U. S. P. VIII (page 34), oxidation of the liquid with a heated copper spiral, is that of Scudder and Mulliken (*Amer. Chem. Jour.*, 21, 266), and is far from being dependable, due to the fact that, as noted by Deghuee (U. S. Dept. of Agr., Bureau of Chemistry, *Bull.* 99, 53) and others, ethyl alcohol will form traces of formaldehyde if the oxidation is carried too far and, thus methyl alcohol might be indicated where none was present.

The suggestion of Sieker (*The Druggists Circular*, March 1901, 65), to heat the alcoholic liquid and then use the heated copper spiral to oxidize the vapor above the liquid and note whether there is produced an irritating vapor, which acts upon the mucous membrane and is characteristic of formaldehyde, would be satisfactory were it not for the fact that pure ethyl alcohol very frequently responds faintly to this test.

Without going any further into the subject, it is sufficient to say that all of these copper spiral tests as now applied are unsatisfactory.

Skilled analysts recognizing this fact employ the Trillat test (*Analyst*, 24, 13, 211-212, 1899); that of Riche & Bardy (Allen's "Commercial Organic Analysis,"

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