

only extended the hospitality of publication to me for the last 22 years, but has also afforded me assistance from the Government Grant placed at its disposal.

It is now my good fortune to have been able to found a Research Institute, from which the present paper forms the first instalment of work. It is my wish that the facilities of this Institute should be available to research workers from all countries. In this I am attempting to carry out the tradition of my country, which, so far back as 25 centuries ago, welcomed scholars from all parts of the world within the precincts of its ancient seats of learning at Nalanda and at Taxilla.

*Investigations dealing with the State of Aggregation. Part IV.—
The Flocculation of Colloids by Salts containing Univalent
Organic Ions.*

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Theory and Scope of the Researches.

In an earlier paper* the action of salts in a heterogeneous system was discussed, and the factors which exert influence on the state of hydration and aggregation of the "colloid phase" were summarised. The present communication deals with only one of these factors, viz., the surface-tension of the solutions and the relationship between this property and the capacity of salts for flocculating colloids.

The mechanism by means of which this flocculation is produced is still a matter of considerable controversy. The view which appears, up to the present, to be most widely maintained is that the precipitation depends, in the first instance, on the adsorption of the active (precipitating) ion by the colloid. According to Freundlich, who is mainly responsible for what may be termed the adsorption hypothesis,† the action of the ions can be explained

* Schryver and Hewlett, 'Roy. Soc. Proc.,' B, vol. 89, p. 361 (1916). For Parts I–III of this series see 'Roy. Soc. Proc.,' B, vol. 83, pp. 96, 113, 119 (1910).

† Freundlich, 'Zeitsch. Physikal. Chem.,' vol. 73, p. 385 (1910); Freundlich and Gann, 'Kolloid-chem. Beihefte,' vol. 8, p. 108 (1916).

in the following manner: Before coagulation takes place, the colloidal particles must lose a certain part of their charge, so that the difference of potential between colloid and dispersion medium does not exceed a certain critical maximum (Powis*). This partial discharge can be brought about, when the precipitating capacity of various salts is considered, by the adsorption of equivalent quantities of ions with a charge opposite to that of the colloids; if one particular active ion is more readily adsorbed by a colloid than another of equal valency, a salt containing the former ion will produce the degree of discharge necessary for flocculation in a lower concentration of solution than will the salt which contains the ion that is less readily adsorbed. By means of the adsorption hypothesis, Freundlich has endeavoured to explain the numerical relationship between the flocculating capacities of salts containing ions of different valencies.† The greater precipitating capacity of salts containing organic ions as compared with those containing inorganic ions has also been explained by the assumption that the former are more readily adsorbed than the latter. Furthermore, typical adsorption isotherms have been obtained, when the distribution of salts between colloid and dispersion medium has been determined.‡

A totally different conception has been put forward by Duclaux,§ who regards the colloid particle as a micella containing a "granule" of the colloid proper associated with "active" ions derived from a substance used in the preparation of a colloidal solution. Thus, in the case of the ferric hydroxide sol, prepared by the dialysis of a solution of ferric hydroxide in ferric chloride, the granules consist of ferric hydroxide, and they are associated with active chlorine ions, and flocculation on addition of a salt is regarded as taking place by the substitution of the active ions by equivalent quantities of others by a purely chemical reaction. It is not necessary to discuss in detail Duclaux's hypothesis, as certain of his assumptions are no longer tenable, as, for example, those dealing with the osmotic pressure of colloidal solutions, which are not in accord with subsequent researches of Perrin on the equipartition of energy in solutions.

More recently still, Pauli and Matula|| have put forward a somewhat different hypothesis, according to which flocculation is regarded as due mainly to a chemical action. Their conceptions are founded on a study of the ferrie

* 'Zeitsch. Physikal. Chem.,' vol. 89, p. 195 (1914).

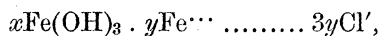
† Freundlich, 'Kapillarchemie,' Leipzig, 1909, pp. 354-355.

‡ See e.g. Maffia, 'Kolloid-chem. Beihefte,' vol. 3, p. 85 (1911), and Gann, *ibid.*, vol. 8, p. 63 (1916).

§ 'Journ. Chim. Physique,' vol. 5, p. 29 (1907), and vol. 7, p. 405 (1909).

|| 'Kolloid Zeitsch.,' vol. 21, 49 (1917).

hydroxide sols, which they regard as complex salts; that prepared from ferric chloride solutions they conceive as being built up according to the formula



and as being a moderately strong electrolyte. On addition of a salt containing an anion in common, *e.g.*, sodium chloride, the dissociation of the colloid is depressed. The coagulating power of other electrolytes appears to be determined by the solubility product of the colloid ion and the anion of the coagulant. The depression of the dissociation is associated with instability of the sol. The conceptions of Pauli and Matula are founded mainly on what appear to be careful electrometric measurements of chlorine and hydrogen ion concentration, but it must be urged in criticism of these, that their value is uncertain when applied to what are undoubtedly heterogeneous systems.

Now if the flocculation of colloids by salts is due, in the first instance, to an adsorption process, some relationship between the flocculation concentration and the surface tension of the salt solutions should be expected; the lower the surface tensions of the solutions, the greater should be the precipitating power. If, on the other hand, a double decomposition involving the "active" ion of the colloid and the corresponding ion of the precipitant, as postulated in the conceptions of Pauli and Matula and of Duclaux, is an essential feature, no such relationship should exist. In the latter case, furthermore, the relative precipitating capacity of salts belonging to a series should vary from colloid to colloid.

To investigate the relationship between surface tension of salt solutions and their capacity for flocculating colloids, salts containing organic ions were chosen, as their normal solutions display wide variations in the first-named property. A certain number of isolated experiments on flocculation by such salts have been published in the literature, but no systematic examination on a wide basis has been recorded.*

For the present work, a series of sodium salts was selected in the first instance, which had been previously employed in determining the relationship between surface tension and disaggregating power. This included the following, which are placed in order of diminishing surface tension of their normal solutions: Formate > acetate > lactate > monochloracetate > dichloracetate > trichloracetate > salicylate > benzoate. The disaggregating action of these salts shows a close relationship with the surface tension of

* See *e.g.*, Freundlich, 'Zeitsch. Physikal. Chem.,' vol. 44, p. 144 (1903); Picton and Linder, 'Trans. Chem. Soc.,' vol. 87, pp. 1922 (1905); Traube and Onodera, 'International. Zeitsch. für Physik.-chem. Biologie,' vol. 1 (1914).

their solutions, those with the lowest surface tensions exhibiting the greatest disaggregating action.*

The disaggregating power has been determined in the following instances : (1) As regards their power of dispersing the globulins (this series, Part I). (2) Their action on inhibiting the formation of methylene iminopeptones (this series, Part II). (3) Their influence on the critical solution temperatures of phenol and water, and their effect on the solubility of certain salts in water (this series, Part III).† In the form of calcium salts these acids also exhibit an inhibiting action on the formation of the cholate gel when the surface tensions of the solutions is lower than that of pure water ; in this case, the greater the concentration, the greater would be the time required for clot formation if the lowering of surface tension impeded aggregation ; the increase in the concentration of the calcium ions, however, diminishes the time, the calcium and anions acting antibatically. In spite of this fact, however, the general relationship between surface tension and disaggregating capacity is clear from the experiments.‡

The above mentioned salts form, therefore, a perfectly well-defined "series" as regards their disaggregating capacity, and it was of special interest to ascertain whether their power for flocculating colloids ran in any parallel with this action. One other sodium salt was added to the number investigated, viz., that of benzene sulphonic acid. This belongs to a class of salts exhibiting, what Neuberg terms "hydrotropic" phenomena,§ that is, the capacity of rendering certain substances soluble in water which are only very slightly soluble in the absence of salts. A similar phenomenon was recorded by one of the authors (see this series, Part III), and ascribed by him to the effect of the salt in lowering the surface tension of the aqueous solution and thus markedly increasing the disaggregating power of the solvent. It is recorded in the sequel that the normal solution of sodium benzene sulphonate has a very low surface tension. Benzene sulphonic acid is, furthermore, a strong acid as compared with salicylic acid, and, for this reason alone, the addition of its sodium salt to the list of those investigated was desirable.

As both negative and positive sols were included in these researches, and as the former are more sensitive to the action of the cations and the latter to

* There is very little difference between the surface tensions of the normal benzoate and salicylate solutions. The latter, which has a slightly greater surface tension in normal solution, has a greater disaggregating power, which may be ascribed to the differences in the viscosity. For discussion on these points, see Part I of this series.

† 'Roy. Soc. Proc.,' B, vol. 83, pp. 96, 113, 119 (1910).

‡ Schryver, 'Roy. Soc. Proc.,' B, vol. 87, p. 366 (1914).

§ 'Biochem. Zeitsch.,' vol. 76, p. 107 (1916).

the anions, it was necessary to investigate in addition the influence of the surface tension of solutions of a series of salts containing a common anion. For this purpose the hydrochlorides of organic bases were chosen. As many of these have only a low basic dissociation constant, their hydrochlorides undergo an appreciable amount of hydrolytic dissociation in water, and this introduces a complication which it is desirable to avoid. For this reason, only those bases are included within the sphere of investigation, of which the basic dissociation constants are greater than that of ammonia.*

Before proceeding to discuss the results obtained, it is necessary to refer to another possible influence of the action of the surface tension of solutions on the process of aggregation of colloids. If adsorption is the main factor in production of the flocculation, it would follow that the lower the surface tension the smaller the concentration of the salt solution necessary to produce the requisite amount of discharge and consequent aggregation. The lowering of the surface tension at the interface colloid-dispersion medium might conceivably tend to act against aggregation, so that two possible actions might be ascribed to the surface tension effect, which are anti-batic. Zsigmondy, however, in a very recent paper,† has expressed the opinion that surface tension effects play but little part in the aggregation in the case, at any rate, of the suspensoid colloids, and that the process takes place by direct attraction of the colloids particles as soon as the potential difference between these and the dispersion medium has been reduced below a certain critical maximum.‡ The dynamics of aggregation has been mathematically treated on this assumption by the late E. von Smoluchowski, and forms the subject of one of the last papers published by him before his death.§ Under any circumstances, the surface tension at the interface suspensoid colloid-dispersion medium is probably high, and the relative amount of lowering produced by the addition of the quantity of salt necessary to bring about aggregation is so small that the mechanical effect of surface tension acting against flocculation is probably quite negligible. This supposition is borne out by experiments recorded in the sequel.

As a general result of these investigations, it was found that there is generally no relationship between the surface tensions of solutions of salts and their flocculating capacity. In the case of positive sols, wide variations were found in the precipitating capacity of the sodium salts, as in these

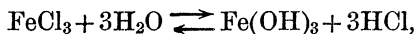
* Reference was made to Lundén's tables for this constant; no record was found of K_b for hexylamine. From analogy one would judge that it is of the same order as that of ammonia.

† 'Zeitsch. Physikal. Chem.,' vol. 92, p. 600 (1918).

‡ 'Zeitsch. Physikal. Chem.,' vol. 92, p. 129 (1917).

§ Powis, *loc. cit.*

cases the active ion is the cation; on the other hand, the precipitating capacity of the hydrochlorides of bases varied only within narrow limits in spite of the wide variations in the surface tension of the normal solutions. In the case of the negative sols wide variations were observed in the action of the hydrochlorides but not in the case of sodium salts. The ferric hydroxide sol was flocculated more readily by the sodium salts of weak acids than by the corresponding salts of strong acids, and the same fact holds, though with some exceptions, to the action of these salts on other sols prepared by the dialysis of salts of inorganic acids. These facts might suggest that in the case of the ferric hydroxide sol the colloidal phase might consist of a heavily hydrated ferric hydroxide (*cf.* researches of van Bemmelen) holding ferric chloride, water, and hydrochloric acid in chemical equilibrium with one another:—



and that the sodium salt of a weak acid would react with the hydrochloric acid with the formation of sodium chloride and a free slightly dissociated organic acid and thus lead to the discharge of the colloid phase. Until more is known, however, as to the distribution of electrolytes between a hydrated colloid phase and the dispersion medium, a problem which involves the consideration of several factors (see Schryver and Hewlett *loc. cit.*), discussion on this matter is of little value. The results found generally do not support the adsorption hypothesis of the flocculating action.

In only one case, and the exception appears to be an important one, is there any marked relationship between the surface tension of the salt solution and the flocculating capacity of the salts, and it is that of the action of the hydrochlorides on the flocculation of mastic. In this case the salts giving solutions with the lower surface tensions have the greater precipitating power. Only one salt, viz., tetraethylammonium chloride falls out of the series and this is different chemically from the hydrochlorides.

This fact seems to suggest that a differentiation may be made between the various suspensoids colloids which takes into account the origin of the electrical charge. In the case of a sol such as ferric hydroxide, the stability depends upon the association of the sol with "active" ions, derived from the salt from which the colloid is prepared (Cl' ions when ferric hydroxide sol is prepared from ferric chloride, and NO_3' ions when prepared from the nitrate). As the ions are gradually removed by hydrolysis, the stability of the sol decreases. Aggregation resulting finally in flocculation is here accompanied by a marked change in the components of the colloid phase. But it is conceivable that sols can exist in which the charge is due to ions

belonging to the molecule of the substance itself, which is the main or perhaps the only body, apart from water of hydration, in the colloid phase. The colloid may be, *e.g.*, an acid substance containing carboxyl groups which will dissociate into readily diffusible hydrogen ions and large slightly diffusible cations. The former would then exist in the outer layers of the colloid phase, and be held electrostatically to the slowly moving cation in the inside. Mastic (a resin acid) is probably the only substance investigated which would form a sol of this class, and it is noteworthy that in this case only is there a close relationship between the surface tensions of their solutions and the flocculating capacity of salts. It is proposed to designate colloids of this class as *endionic* and those of the other class *exionic*. It is hoped, at a more favourable opportunity, that these investigations may be extended to other substances, such as the proteins, which probably belong to this class. Pressure of other work and difficulty in obtaining the requisite materials are, for the moment, obstacles to such an extension.

Surface Tensions of Normal Solutions.

The materials employed were, when obtainable, Kahlbaum's preparations. The dichloroacetic acid was prepared in the laboratory from chloralhydrate by Wallach's method. The lactic acid was obtained from a crude commercial specimen by recrystallisation of the calcium salt and its subsequent decomposition by anhydrous oxalic acid (in slight deficiency) in pure ether. Mono- and trimethylamine were obtained in a satisfactory state of purity as hydrochlorides by a method recently described by Werner.* The corresponding salt of dimethylamine, in spite of several attempts, could not be obtained pure by Werner's method, and the base was finally prepared by the action of sodium hydroxide on dimethylaniline. The authors are indebted to Prof. Philip for a sample of triethylamine and tetraethylammonium bromide, from which latter substance the chloride was prepared in the usual manner. The surface tensions of the sodium salts are quoted from the first paper of this series, with the exception of that of benzene sulphonic acid. The surface tensions of this and the other substances in the Table were determined by the drop method with the use of a Traube stalagmometer. The specific gravities were determined in a small pycnometer. The sodium salt solutions were made by the method described in the first paper. The chloride solutions were standardised by silver nitrate. The usual precautions for obtaining sufficiently pure water were taken.

* 'Trans. Chem. Soc.,' vol. 111, p. 844 (1917).

Surface Tensions of Normal Salt Solutions. $\gamma_{H_2O} = 1$.

Sodium Salts.

(Hydro) Chlorides.

1	Sodium chloride	1·032	I	Sodium chloride	1·032
2	Sodium formate	1·020	II	Ammonium chloride	1·027
3	Sodium lactate	1·013	III	Monomethylamine hydrochloride	1·017
4	Sodium acetate	1·004	IV	Trimethylamine hydrochloride ...	1·0074
5	Sodium monochloracetate ...	1·002	V	Dimethylamine hydrochloride ...	1·006
6	Sodium dichloracetate	0·970	VI	Tetraethylammonium chloride	0·965
7	Sodium trichloracetate	0·905	VII	Piperidine hydrochloride	0·953
8	Sodium salicylate	0·902	VIII	Triethylamine hydrochloride	0·950
9	Sodium benzoate	0·897	IX	Benzylamine hydrochloride	0·878
10	Sodium benzene sulphonate	0·816	X	Isoamylamine hydrochloride	0·728
			XI	Hexylamine hydrochloride	0·516

Stalagmometer and pycnometer readings were taken at 15° C.

Flocculation Capacity of Salts.

Attempts were made to carry out the precipitation under as nearly as possible constant conditions. To 2 c.c. of the sol in a series of small test-tubes were added 2 c.c. of various dilutions of the salt in concentrations diminishing in geometrical ratio. The salt solution was rapidly poured into the sol and the mixture was then poured back into the first test-tube. The limits between which precipitation took place were then noted after several hours. The finer limits were then determined by carrying out the precipitation with a number of dilutions between the coarser limits, and the second set of experiments were carried out at constant temperature (20°), the salt solutions and sols being kept at this temperature before mixing. The observations were generally made after an interval of 17 hours. In the following Tables the numbers refer to the dilutions of the salts (after mixing with the sols) in millimols per litre. +++ indicates complete precipitation, ++ not quite complete precipitation, + slight turbidity, 0 no change in sol visible to naked eye. In certain cases the finer limits were not determined, especially when these were high, as larger amounts of costly materials necessary for the experiment were not available.

Ferric Hydroxide.

Prepared by dilution of *liquor ferri dialysat.* B.P., diluted with seven times the volume of water. 100 c.c. contained 1·33 per cent. solid, dried at 100° C.

Sodium Salts.

						0.			
Formate	12.5	+++	10.93	++	9.37	++	7.82	+	7.03
Lactate	7.82	+++	7.03	++	6.25	++	5.64	+	4.60
Acetate	5.46	+++	4.60	++	3.90	+			3.51
Monochloracetate	18.75	+++	15.62	++	14.06	++	12.50	+	10.93
Dichloracetate	56.25	+++	50.0	++	43.75	+			37.50
Trichloracetate	56.25	+++	50.0	++	43.75	++	37.5	+	31.25
Salicylate	2.69	+++	2.30	++					1.95
Benzoate	3.51	+++	3.12	++	2.69	+			2.30
Benzene sulphonate	21.87	+++	18.75	++					15.62

(Hydro) Chlorides.

		0.
Sodium	250 + + +	125
Ammonium	250 + + +	125
Monomethylamine	250 + + +	125
Trimethylamine	250 + + +	125
Dimethylamine	250 + + +	125
Tetraethylammonium	125 + + +	112.5
Piperidine	250 + + +	125
Triethylamine	250 + + +	125
Benzylamine	250 + + +	125
Isoamylamine	250 + + +	125
Hexylamine	250 + + +	125

Zirconium Hydroxide.

Prepared by repeated evaporation of Zirconium nitrate solution by Müller's* method. 100 c.c. contained 1.93 per cent. solid, dried at 100° C.

Sodium Salts.

									0.								
Formate	56.25	+	+	+	50.0	+	+	43.75	+	37.5	+	31.5					
Lactate	—											> 500					
Acetate	62.5	+	+	+	56.25	+	+	50.0	+	+	43.75	+	37.5	+	31.25		
Monochloracetate ...	56.25	+	+	+	50.0	+	+	43.75	+	+	37.5	+	31.25				
Dichloracetate	50.0	+	+	+	43.75	+	+						37.50				
Trichloracetate	43.75	+	+	+	37.5	+	+						31.25				
Salicylate	14.06	+	+	+	12.5	+	+	9.37	+	+	7.82	+	7.63	+	6.25		
Benzoate	12.5	+	+	+	10.93	+	+	9.37	+	+	7.82	+	7.03	+	9.25		
Benzene sulphonate	225	+	+	+	200	+	+	175	+	+	150	+	125	+	112.5	+	100.0

(Hydro) Chlorides.

No flocculation produced at a strength of 500 millimols per litre.

* 'Zeitsch. Anorg. Chem.,' vol. 52, p. 316 (1907).

Cerium Hydroxide.

Prepared by dialysis of ceric ammonium nitrate by Biltz's method.*
100 c.c. contained 0.049 per cent. solid, dried at 100° C.

Sodium Salts.

		0.
Formate	0.46 + + + 0.38 +	0.31
Lactate	0.23 + + + 0.19 + + 0.17 + + 0.15 +	0.13
Acetate	0.46 + + + 0.38 + + 0.35 +	0.31
Monochloracetate	0.53 + + + 0.46 + + 0.38 + + 0.35 + +	0.31
Dichloracetate	1.87 + + + 1.56 + + 1.40 + + 1.25 +	1.09
Trichloracetate	1.87 + + + 1.56 + + 1.40 +	1.25
Salicylate	0.19 + + + 0.17 + + 0.15 + + 0.13 +	0.11
Benzoate	0.23 + + + 0.19 + + 0.17 + + 0.15 + 0.13 +	0.11
Benzene sulphonate	1.25 + + + 1.09 + +	0.93

(Hydro) Chlorides.

		0.
Sodium	3.75 + + + 3.18 + + 2.81 + + 2.43 + + 2.18 + 1.87 +	1.56
Ammonium	3.75 + + + 3.18 + + 2.81 + + 2.43 +	2.18
Monomethylamine	4.37 + + + 3.75 + + 3.18 + + 2.43 + + 2.18 + 1.87 +	1.56
Trimethylamine	2.81 + + + 2.43 + + 2.18 + + 1.87 + + 1.56 +	1.40
Dimethylamine	3.75 + + + 3.18 + + 2.18 + + 2.43 + + 2.18 + + 1.87 +	1.56
Tetraethylammonium	2.43 + + + 2.18 + + 1.87 + + 1.56 + + 1.40 +	1.09
Piperidine	3.75 + + + 3.18 + + 2.81 + + 2.43 + 2.48 +	1.87
Triethylamine	5.63 + + + 5.0 + + + 4.37 + + 3.75 + 3.18 + 2.81 + 2.43 + 2.18 +	1.87
Benzylamine	3.75 + + + 3.18 + + 3.81 + + 2.43 +	2.18
Isoamylamine	4.37 + + + 3.75 + + 3.18 + 2.81 + 2.43 + 2.18	1.87
Hexylamine	3.18 + + + 2.81 + + 2.43 + + 2.81 +	1.56

Victoria Blue B. (Badische Company.)

Solution dialysed for four days. 100 c.c. contained 0.094 solid, dried at 100° C.

Sodium Salts.

		0.
Formate	112.5 + + + 100 +	87.5
Lactate	225 + + + 200 + + 175 +	150
Acetate	125 + + 112.5 +	100
Monochloracetate	56.15 + + + 50.0 + + 43.75 + + 37.5 +	31.25
Dichloracetate	14.06 + + + 12.5 + + 10.93 + + 9.37 + 7.82 + +	7.03
Trichloracetate	1.95 + + 1.436	0.97
Salicylate	0.97 + + 0.68 +	0.48
Benzoate	14.06 + + + 12.5 + + 10.93 + 7.82 +	7.03
Benzene sulphonate	1.95 +	1.86

* 'Berl. Berichte,' vol. 35, p. 4435 (1902).

(Hydro) Chlorides.

			0.
Sodium	112·5 + + + 100	+ + 87·5 + + 75 + +	62·5
Ammonium	112·5 + + + 100	+ + 87·5 +	75·0
Monomethylamine	112·5 + + + 100	+ + 87·5 + + 75 +	62·5
Trimethylamine	112·5 + + + 100	+ + 87·5 + + 75 +	62·5
Dimethylamine	112·5 + + + 100	+ + 87·5 + + 75 +	62·5
Tetraethylammonium	21·87 + + + 18·75 + + 15·62 + +		14·06
Piperidine	112·5 + + + 100	+ + 87·5 + 75 +	62·5
Triethylamine	112·5 + + + 100	+ + 87·5 + 75 +	62·5
Benzylamine	112·5 + + + 100	+ + 87·5 + 75 +	62·5
Isoamylamine	112·5 + + + 100	+ + 87·5 + 75 +	62·5
Hexylamine	112·5 + + + 100	+ + 87·5 + 75 +	62·5

Azo Blue. (Bayer Company.)

Solution dialysed for three days. 100 c.c. contained 0·025 per cent. solid, dried at 100° C.

Sodium Salts.

		0.
Formate	175 + + + 150 + + 125 + + 112 + 100 +	87·5
Lactate	200 + + + 175 + + 150 + + 125 + 112·5 +	75·0
Acetate	200 + + + 175 + + 150 + + 125 + 112·5 +	75·0
Monochloracetate	175 + + + 150 + + 125 + + 112·5 + 100 +	87·5
Dichloracetate	200 + + + 175 + + 150 + + 125 + 112·5 +	100
Trichloracetate	150 + + + 125 + + 112·5 + + 100 + + 87·5 +	75·0
Salicylate	200 + + + 175 + + 150 + + 125 + 112·5 +	87·5
Benzoate	200 + + + 175 + + 150 + + 125 + 112·5 +	87·5
Benzene sulphonate	175 + + + 150 + + 125 + 112·5 +	100

(Hydro) Chlorides.

		0.
Sodium	200 + + + 175 + + 150 + + 125 +	75·0
Ammonium	100 + + + 87·5 + + 75 +	62·5
Monomethylamine	112·5 + + + 110 + + 87·5 + + 75 +	62·5
Trimethylamine	112·5 + + 112·5 + 100 +	87·5
Dimethylamine	125 + + + 112·5 + + 100 + 87·5 +	75·0
Tetraethylammonium ...	500 +	250·0
Piperidine	87·5 + + + 75 + + 625 + + 56·25 + +	31·25
Triethylamine	250 + + + 225 + + 200 + + 175 +	125·0
Benzylamine	15·62 + + + 14·06 + + 12·5 + + 10·93 +	7·82
Isoamylamine	21·87 + + + 18·75 + + 15·65 + 14·06 +	10·93
Hexylamine	9·37 + + + 7·82 + + 7·08 + + 6·25 + +	4·60

Brilliant Congo R. (Berlin Actien-Gesellschaft.)

100 c.c. contained 0.14 per cent. solid, dried at 100° C.

Sodium Salts.

		0.
Formate	500 + + +	250
Lactate	500 + + +	250
Acetate	500 + + +	250
Monochloracetate	500 + + +	250
Dichloracetate	500 + + +	250
Trichloracetate	500 + + +	250
Salicylate	500 + + +	250
Benzoate	500 + + +	250
Benzene sulphonate	500 + + +	250

(Hydro) Chlorides.

		0.
Sodium	500 + + +	250
Ammonium	—	>500
Monomethylamine	—	>500
Trimethylamine	—	>500
Dimethylamine	—	>500
Tetraethylammonium	—	>500
Piperidine	—	>500
Triethylamine	—	>500
Benzylamine	500 + + + 250 + +	125
Isoamylamine	—	>500
Hexylamine	200 + + + 125 + + 62.5 + +	31.25

Zsigmondy's Scarlet Gold sol.

Prepared by Zsigmondy's method* by reducing gold chloride with formaldehyde.

Sodium Salts.

	Strength in millimols per litre giving change in colour.	r.
Formate	21.87 b, 18.75 m	15.62
Lactate	28.12 b, 25 m, 21.87 m	18.75
Acetate	21.87 b, 18.75 m	15.62
Monochloracetate	25 b, 21.87 m	18.75
Dichloracetate	18.75 b, 15.62 m, 14.06 m	12.5
Trichloracetate	18.75 b, 15.62 m	14.06
Salicylate	25 b, 21.87 m, 18.75 m	15.62
Benzoate	31.25 b, 28.12 m, 25 m, 21.87 m, 18.75 m	15.62
Benzene sulphonate	37.5 b, 31.25 m, 28.12 m	25.0

b = blue; m = mauve; r = red.

* 'Zeitschr. f. Electro-Chem.,' vol. 4, p. 546 (1898).

Hydrochlorides.

	Strength in millimols per litre giving change in colour.	r.
Sodium	28·12 b, 25·0 m, 21·87 m	18·75
Ammonium	15·62 b, 14·06 m, 12·5 m	10·93
Monomethylamine	15·62 b, 14·06 m	12·50
Trimethylamine	9·37 b, 7·82 m, 7·03 m	6·25
Dimethylamine	15·62 b, 14·06 m	12·50
Tetraethylammonium	10·93 b, 9·37 m, 7·82 m, 7·03 m	6·25
Piperidine	9·37 b, 7·82 m, 7·03 m	6·25
Triethylamine	4·60 b, 3·90 m, 3·51 m	3·12
Benzylamine	3·90 b, 3·51 m	3·12
Isoamylamine	9·37 b, 7·82 m, 7·03 m, 6·25 m	5·46
Hexylamine	3·12 b, 2·69 m, 2·30 m	1·95

b = blue; m = mauve; r = red.

Arsenic Sulphide.

Prepared by the method of Picton and Linder. 100 c.c. contained 0·31 per cent. solid, dried at 100° C.

Sodium Salts.

		0.
Formate	112·5 + + + 100 +	87·5
Lactate	125 + + + 112·5 + + 100 +	87·5
Acetate	125 + + + 112·5 + +	100·0
Monochloracetate	112·5 + + + 100 + + 87·5 + 75·0 +	62·5
Dichloracetate	100 + + + 87·5 + +	75·0
Trichloracetate	112·5 + + + 100 + + 87·5 +	75·0
Salicylate	100 + + + 87·5 + + 75 + +	62·5
Benzoate	125·0 + + + 112·5 +	100·0

Hydrochlorides.

		0.
Sodium	100 + + + 87·5 + + 75·0 +	62·5
Ammonium	56·25 + + + 55·0 + + 43·75 +	37·5
Monomethylamine	37·5 + + + 31·25 + + 28·12 + + 25 + + 21·87 +	18·75
Trimethylamine	14·06 + + + 12·5 + + 10·93 + 9·73 +	7·82
Dimethylamine	21·87 + + + 18·75 + + 15·62 + 14·06 +	12·50
Tetraethylammonium	22·30 + + + 1·95 + + 1·75 + + 1·56 + 1·36 +	0·97
Piperidine	6·25 + + + 5·46 + + 4·6 + + 3·9 + + 3·12 +	2·69
Triethylamine	2·69 + + + 2·30 + + 1·95 +	1·75
Benzylamine	3·51 + + + 3·12 + + 2·69 + + 2·20 +	1·95
Isoamylamine	6·25 + + + 5·46 + + 4·60 + + 3·90 +	3·51
Hexylamine	3·51 + + + 3·12 + + 2·69 + + 2·30 +	1·95

Mastic.

One hundred cubic centimetres contained 0·13 per cent. solid, dried at 100° C.

Sodium Salts.

		0.
Formate	500 + + + 250 +	125
Lactate	500 +	250
Acetate	500 + +	250
Monochloracetate	500 + + + 250 + +	125
Dichloracetate	500 + + + 250 +	125
Trichloracetate	500 +	250
Salicylate	500	250
Benzoate	500	250
Benzene sulphonate	—	>500

(Hydro) Chlorides.

		0.
Sodium	112·5 + + + 100 + + 87·5 + + 75 +	62·5
Ammonium	75 + + 62·5 +	56·25
Monomethylamine	87·5 + + + 75 + + 62·5 +	56·25
Trimethylamine	62·5 + + 56·25 +	50·0
Dimethylamine	87·5 + + + 75 + + 62·5 +	56·25
Tetraethylammonium	—	>500
Piperidine	28·12 + + + 25 +	21·87
Triethylamine	28·12 + + + 25 + + 21·87 + 18·75 +	15·62
Benzylamine	14·06 + + + 12·5 + + 10·93 +	9·37
Isoamylamine	14·06 + + + 12·5 + + 10·93 +	9·37
Hexylamine	5·64 + + + 4·60 +	3·90

The following Table gives a summary of the chief results obtained.

The numbers indicate the salt solutions, the Arabic numerals representing the sodium salts, and the Roman numerals the hydrochlorides, the smaller numbers being given to those solutions with the higher surface tensions.

The numbers follow one another in the vertical columns in the order of their diminishing flocculating power.

The solutions with equal flocculating power are bracketed together.

Ferrie hydroxide.	Zirconium hydroxide.	Cerium hydroxide.	Victoria blue.	Azo blue.	Brilliant Congo R.	Gold.	Arsenic sulphide.	Mastic.
8	{ 9	{ 9	8	XI	XI	{ XI	VI	{ XI
9	{ 8	{ 8	7	IX	IX	{ IX	IV	{ X
4	{ 7	{ 3	10	X	I	{ VIII	IX	{ IX
3	{ 5	{ 5	{ 9	VII	X	{ X	{ XI	{ VIII
2	{ 4	{ 4	{ 6	{ III	{ VIII	{ VII	{ VII	{ VII
5	{ 2	{ 2	5	{ II	{ VII	{ VI	X	{ V
10	6	10	1	{ V	{ VI	{ IV	IV	{ IV
7	10	6	2	{ I	{ V	{ II	V	{ III
6	3	7	3	IV	IV	V	III	{ II
1	1	1	4	VIII	III	III	II	{ I
				VI	I	I	I	{ VI

Summary.

The theories regarding the flocculation of colloids by salts have been discussed. To test the "adsorption hypothesis," the precipitating capacity of salts containing organic ions, the normal solutions of which exhibit wide variations in their surface tensions, was determined. It was expected, should this hypothesis hold, that the salts giving solutions of lowest surface tension would exhibit the greatest flocculating capacity. The following sodium salts were employed: formate, acetate, lactate, mono-, di- and trichloracetate, salicylate, benzoate, and benzene sulphonate. Also the following (hydro) chlorides: sodium, ammonium, monomethylamine, trimethylamine, dimethylamine, tetraethylammonium, piperidine, triethylamine, benzylamine, isoamylamine, hexylamine. The following sols were used: ferric, zirconium and ceric hydroxides, Victoria blue B, azo-blue, brilliant Congo-red R, scarlet gold sol, arsenic sulphide, and mastic.

In general, no relationship was found to exist between the surface tensions of the normal solutions and the flocculating capacity of salts. When a series of salts was compared in which the varying ion was not the active precipitating ion, the precipitating limits were all within a comparatively narrow range, in spite of the wide variations of the surface tensions of the solutions. In the series, when the varying ion was the active ion, the range was large, although the precipitating capacity could not be generally correlated with the surface tension. The marked exception to this statement was shown in the case of mastic, when precipitated by the (hydro)chlorides. In this case the salts of low surface tension exhibit the greater flocculating power (with the exception of tetraethylammonium chloride).

It is suggested that suspensoid colloids may be subdivided into classes: (a) those, like ferric hydroxide, which owe their charge to association with "active" ions derived from salts from which they have been prepared, which are removed during aggregation, which results finally in flocculation, and which may be termed "exionic colloids;" (b) those owing their charge to the dissociation of the colloid itself, in which a rapidly diffusing ion (such as hydrogen ion) forms the outer layer, and is held electrostatically to a less diffusible ion. These may be termed "endionic colloids." Mastic is probably a colloid which belongs to this class.
