164. *Ionic Interchange in Sulphur Sols. Part III. The Mechanism of Coagulation.*

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INVESTIGATION of the influence of salts upon the stability of sulphur sols (Bolam and Bowden, J., 1932, 2864; Bolam and Muir, J., 1933, 1022) has shown that the coagulation value of a salt is markedly dependent upon (1) the valency and lyotropic character of its kation, (2) the temperature, (3) the alcohol content and (4) the acidity of the sol, and

(5) the nature of the anions present. The effect of any one of these factors is found to correspond closely to the extent to which the hydrogen of the micellar polythionic acid is replaced by the kations of the salt, under the given conditions. It would thus appear that, at least in the case of these sulphur sols, the ionic interchange is an essential part of the mechanism of coagulation, and not simply a process which is incidentally involved (cf. Verwey and Kruyt, *Z. physikal. Chem.*, 1934, *A*, **167**, 312).

EXPERIMENTAL.

Sols.—The sols were prepared as described by Bolam and Muir (*loc. cit.*), *i.e.*, by interaction of sodium thiosulphate and concentrated sulphuric acid, followed by repeated coagulation, initially with sodium chloride and finally with hydrochloric acid. With one exception (J′) the sols were used in the undialysed condition, and hence contained considerable amounts of hydrochloric acid (see Table I).

TABLE I.

Composition of sols.

Sol.	S in sol, g./100 c.c.	After dilution with equal vol. of H_2O. Equiv. concn. HCl.	Micromols. micellar polythionic $H^{\cdot}$ ion per g. S.
G	9·83	0·254	992
H	7·55	0·124	874
J	5·85	0·142	889
J′	2·05	0·00012	136
K	5·47	0·144	1133
L	7·31	0·157	795

To minimise variation in the composition of the sols, they were stored in Jena bottles in the dark. Coarse sulphur very slowly separated, but as the following observations indicate, this was accompanied by no appreciable change in the amount of micellar (" bound ") polythionic acid. (1) 2·0 C.c. of sol J were completely coagulated by 2·0 c.c. of 0·1*M*-barium chloride, and the decrease in barium-ion concentration was determined by the conductivity method already described (Bolam and Muir, *loc. cit.*).

	Sp. condty., mho × 10^6. Before adsorption.	After adsorption.	Decrease in $Ba^{\cdot\cdot}$ ion (equiv./l.).
Fresh sol	2430	1801, 1795	0·0264, 0·0256
Same sol after 2 months	2430	1798, 1818	0·0260, 0·0252

On the second occasion, the concentration of liberated hydrogen ion in the same mixture was found (Expt. *e*) to be 0·026*N*, which agrees well with the figure for maximum adsorption of barium. Since under the given conditions, adsorption of barium ion takes place with liberation of polythionic hydrogen ion only, it follows that the sol underwent no detectable change during these two months. (2) Although about a month elapsed between the determination of the maximum adsorption of barium and the estimation of " bound " polythionic acid in sol F (see Bolam and Muir, *loc. cit.*, Table II), the two agreed within the small experimental error.

Bassett and Durrant (J., 1932, 2946) report that in the sols examined by them, the polythionate was entirely " bound " at first but that 30—50% became " free " in 7—10 days. The proportion of " free " acid in sol G, 3 weeks after preparation, was determined as follows. 5·0 C.c. samples of sol were completely coagulated with potassium chloride, and the coagula filtered off and well washed with potassium chloride solution. The filtrates were treated with sodium hydroxide (final concentration = 0·4*N*) at 25° for various periods of time, then acidified with sulphuric acid and titrated with standard iodine. The data obtained are in line with the observation of Bassett and Durrant that only 95% of the pentathionate is converted into thiosulphate in 2—3 hrs.

	Sample 1.	Sample 2.	Sample 3.
Hrs. treated with NaOH	4·5	5·5	18·5
N/20-iodine required, c.c.	3·67	3·73	4·00
Free pentathionic acid, equiv./l.	0·0147	0·0149	0·0160

It is clear that the titre corresponding to complete reaction must lie close to 4·0 c.c. The " free " polythionic acid was therefore taken as 0·0160 equiv./l. of undiluted sol, which proved to be about only one-sixth of the " bound " acid (two determinations, as silver sulphide, gave 0·097 and 0·098 equiv./l.; also the maximum adsorption of barium was found to be 0·099 equiv./l.). The sols studied by Bassett and Durrant contained principally sodium salts, with only traces of acid, which may account for the different behaviour. Since the total concentration of acid in the intermicellar liquid of sol G, after dilution with an equal volume of water, was 0·254 equiv./l., it is evident that the concentration of hydrochloric acid greatly exceeded that of the " free " pentathionic acid.

Experiment a.—The amounts of hydrogen ion liberated by the chlorides of lithium, potassium, and strontium, when present at the respective concentrations required to produce a given degree of coagulation, were determined as follows. Mixtures of sol K and salt solution, all at the same concentration with respect to sulphur but containing various amounts of salt, were kept for 18 hours in a constant-temperature room at 12·0° ± 0·5°. Since the sol was polydisperse, coagulation took place in stages, and it was found that the coagulated sulphur completely settled out, leaving a transparent yellow supernatant liquid. The intensity of the light scattered by the uncoagulated sulphur in each case was determined by means of a Zeiss nephelometer, used in conjunction with a Pulfrich photometer, and the concentrations of the three salts which gave a certain suitable value of " absolute turbidity " (*i.e.*, turbidity in terms of the standard translucent glass body provided by the makers) ascertained. Table II contains the relevant data. As elsewhere in the paper, salt concentrations (as well as those of total acid and liberated hydrogen ion) are expressed in equivs. per l. of sol–salt mixture. The figures in the last line of the table are mean values of the absolute turbidity.

TABLE II.

Turbidity measurements (Sol K).

Salt	LiCl.			KCl.		$SrCl_2$.		
Concentration	3·51			0·10		0·075	0·070	0·066
Drum readings *	59	63	63	65	65	79	69	62
	61	62	62	65	63	77	70	61
	61	63	63	65	63	78	68	61
		62					68	
Turbidity	0·250			0·243		0·200	0·226	0·256

* Each column gives successive readings for a single sample of supernatant liquid. In the case of lithium chloride, two of the three samples were taken from the same mixture; in the case of potassium chloride, the samples represent two separately prepared mixtures.

Mixtures containing lithium chloride at 3·51, potassium chloride at 0·1, and strontium chloride at 0·066 equiv./l. were ultrafiltered at 12·0° ± 0·5°, after standing at that temperature for 18 hrs., and the total acid in the ultrafiltrates determined by electrometric titration. Ultrafiltration was carried out as described in previous communications (*locc. cit.*), except that the filtrates were collected in a glass receiver which completely enclosed the filter, so that evaporation was reduced to negligible proportions. A constant volume (2·0 ± 0·003 c.c.) of filtrate was titrated with 0·1041N-sodium hydroxide, by means of the quinhydrone electrode, and the titres obtained are given in Table III.

TABLE III.

Liberation of hydrogen ion by lithium, potassium, and strontium chlorides (Sol K).

Salt.	Concentration.	Titre (c.c.).	Total acid.	Liberated $H^{\cdot}$ ion.
LiCl	3·51	3·27, 3·26	0·170, 0·169	0·026, 0·025
KCl	0·10	3·28, 3·26	0·171, 0·169	0·027, 0·025
$SrCl_2$	0·066	3·25, 3·24	0·169, 0·168	0·025, 0·024
KCl	1·00	3·34	0·174	0·030

The mixtures were uniformly prepared by the addition of sol to the same volume of salt solution. In some instances the same mixture was used for both measurement of turbidity and titration (less than 1·0 c.c. was required for the former), but in others a fresh mixture was prepared for the second operation. The titres for the lithium chloride mixture have been corrected for the contraction incident upon dilution of 7·0M-lithium chloride to 3·5M; this correction was found by density measurements to be 0·3%, which is equivalent to about 0·01 c.c. increase in titre. All measurements of volume were made at ordinary room temperature.

In the last column of Table III are given the concentrations of the hydrogen ion displaced from the sulphur micelles. These values were obtained by subtracting the concentration

(0·144 equiv./l.; determined as described under Expt. *b*) of acid obtained by adding water, instead of salt solution, to the sol, from the concentrations of total acid shown in the third column of the table. At a final concentration of 1·0*M*, potassium chloride produced complete coagulation of the sol, and liberated the whole of the polythionic hydrogen. It will be seen that this amounted to 0·030 equiv./l., as determined by titration, which agrees well with the value of 0·031 obtained by the alternative method indicated below (Expt. *b*).

Experiment b.—Mixtures of sol K and potassium chloride, prepared as described in Expt. *a*, were kept for 18 hrs., either in the constant-temperature room at 16·5°, or in a Thermos flask containing ice. The extent of coagulation was then noted, and the amount of liberated hydrogen ion determined by neutralising the bulk of the acid in the supernatant liquid, or ultrafiltrate, with standard alkali, and estimating the small amount of unneutralised acid by means of the glass electrode (see Bolam and Muir,* *loc. cit.*, for details of procedure). Ultrafiltrations were carried out at the same temperatures as the corresponding coagulation experiments. Table IV gives the data obtained.

TABLE IV.

Liberation of hydrogen ion by potassium chloride at 0° *and* 16·5° (*Sol K*).

		At 16·5°.						At 0°.			
Concn. salt.	Stability.	ΔE (mv.).	$a_{\mathrm{H}} \times 10^4$.	Total acid.	Liberated H$^{\cdot}$ ion.	Concn. salt.	Stability.	ΔE (mv.).	$a_{\mathrm{H}} \times 10^4$	Total acid.	Liberated H$^{\cdot}$ ion.
0·375	0	107·3 106·3	78 74	0·175	0·031	0·100	0	106·5 106·4	75 75	0·175	0·031
0·125	0	106·8 106·1	76 74	0·175	0·031	0·088	0	106·5 106·2	75 74	0·175	0·031
0·122	+	106·1 105·1	74 71	0·174	0·030	0·075	+	106·5 105·5	75 72	0·174	0·030
0·050	*u*	114·0 114·2	102 102	0·156	0·012	0·050	*u*	119·1 119·0	126 126	0·162	0·018
Nil	*u*	101·5 99·2	60 55	0·144		Nil	*u*	98·9 98·8	55 55	0·144	

ΔE is the difference between the potential, at 18°, of the glass electrode in 0·05*M*-potassium hydrogen phthalate and in the system : 2·0 c.c. supernatant liquid (or ultrafiltrate) + 1·0 c.c. alkali + 2·0 c.c. potassium chloride solution of the strength required to give a final concentration of 1·0*M* with respect to that salt. It was found that, under the given conditions, a_{H} (the activity of the hydrogen ion, calculated from ΔE in the usual way) was equal in value to the concentration of unneutralised acid in the system. 0·313*N*-Sodium hydroxide was used for neutralisation of a supernatant liquid, and 0·261*N* for an ultrafiltrate. The significance of the stability symbols is as follows : 0 = complete coagulation (clear colourless supernatant liquid which gave no turbidity on the addition of excess of potassium chloride); + = coagulation point (clear colourless supernatant liquid which gave trace of turbidity on the addition of excess potassium chloride); *u* denotes that the mixture was ultrafiltered. In Fig. 1, concentration of liberated hydrogen ion (Table IV, col. 6) is plotted against salt concentration (Table IV, col. 1).

Experiment c.—A series of mixtures was prepared by adding 2·0 c.c. of *x*% (by vol.) ethyl alcohol and 1·0 c.c. of 1·5*M*-sodium chloride to 2·0 c.c. of sol J. These were allowed to stand for 18 hrs. at about 16°, the degree of coagulation observed, and the liberated hydrogen ion determined by electrometric titration with 0·1064*N*-sodium hydroxide. Ultrafiltrations were carried out at 15—16°. The results appear in Table V, the concentrations of total acid and liberated hydrogen ion being calculated, for purposes of comparison, as though the volume

TABLE V.

Liberation of hydrogen ion by sodium chloride in the presence of alcohol (*Sol J*).

x.	Stability.	Titre (c.c.).	Vol. mixture (c.c.).	Total acid.	Liberated H$^{\cdot}$ ion.
0	*u*	2·37, 2·38	5·00	0·157	0·015
25	*u*	2·46, 2·46	4·99	0·163	0·021
50	*u*	2·52, 2·52	4·97	0·166	0·024
75	*u*	2·56, 2·57	4·91	0·167	0·025
100	+/0	2·63, 2·63	4·82	0·168	0·026

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* On p. 1023 of this paper, $E - E'$ should read $E' - E$, and $a_{\mathrm{H}} = 0{\cdot}078$ should read $a_{\mathrm{H}} = 0{\cdot}0078$.

of the mixture was only 4·0 c.c., *i.e.*, the sum of the volumes of sol and salt solution. In the case of the alcohol systems, owing to contraction, the volume was actually somewhat less than 5·0 c.c. (about 4% less when $x = 100$) and allowance has been made for this effect by employing the density values given in the International Critical Tables (Vol. III, 116—119). It was found that 1·0*M*-sodium chloride was necessary to produce complete coagulation in the absence of alcohol.

The figure for total acid at $x = 100$ was checked by further experiments, with the following results.

Concn. NaCl in mixture	0·3*M*.		0·5*M*.	
Time interval before measurement (hrs.)	4	42	3	42
Titre (cf. 2·63 c.c. in Table V)	2·63	2·62	2·62	2·63

Taking all six titres into account, it appears that the maximum concentration of total acid for sol J is 0·168 equiv./l., which is identical with the value obtained by a quite independent method (see Expt. *e*, as also for determination of the maximum concentration of liberated hydrogen ion obtainable, *i.e.*, 0·026 equiv./l.).

FIG. 1.
Sol K (Table IV).

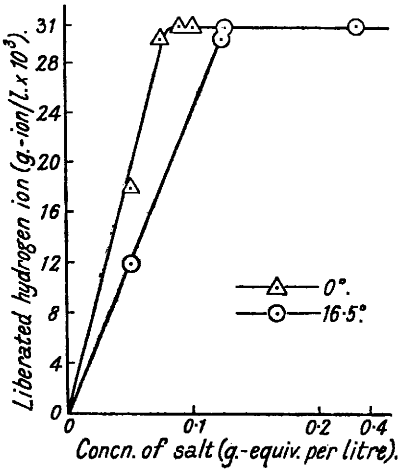
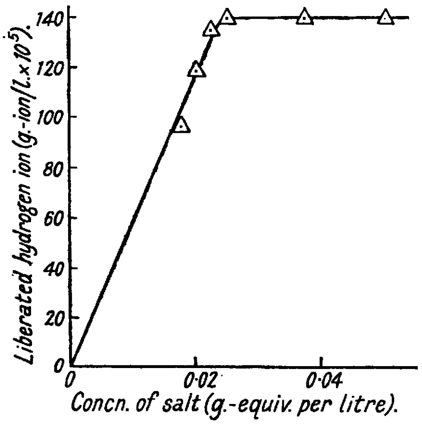


FIG. 2.
Sol J′ (Table VI).



It was thought that selective adsorption of the alcohol, by the cellophane, might occur during ultrafiltration, but special experiments showed that no correction was needed in this respect. 50 Sq. cms. of cellophane were immersed, for some hours, in 10 c.c. of an aqueous-alcoholic solution of barium chloride. Conductivity measurements indicated that no appreciable change in concentration took place.

Concn. alcohol (%)	25	50
Period of immersion (hrs.)	3	22
Cell resistance (ohms)—after contact with cellophane	722·5	459·3
,, ,, —before ,, ,,	722·0	460·5

Experiment d.—A quantity of sol J was dialysed in a collodion bag, suspended in distilled water, until the hydrochloric acid was almost all removed. The degrees of coagulation for various mixtures of 2·0 c.c. of sol (J′) + 2 c.c. of potassium chloride, after standing for 18 hrs. at 16·5° in a thermostat, were ascertained. Since the total concentration of acid was small, the liberation of hydrogen ion was measured directly by the glass electrode, no alkali being added. Except in the case of 1·0*M*-potassium chloride, the cell solution consisted of 2·0 c.c. of supernatant liquid (or ultrafiltrate) + 2·0 c.c. of potassium chloride of such strength that the final concentration was 1·0*M*. At this concentration of the salt, a_H = concentration of acid. All the experiments were duplicated and the mean values obtained are given in Table VI and plotted in Fig. 2. In the case of 0·0225*M*-potassium chloride, the supernatant liquid was quite free from yellow colour, but remained slightly turbid, owing to the presence of a small

TABLE VI.

Liberation of hydrogen ion in acid-free sol (Sol J').

Concn. salt.	Stability.	ΔE (mv.).	p_H.	Total acid $\times 10^5$.	Liberated H˙ ion $\times 10^5$.
1·00	0	66·6	2·82	151	139
0·05	0	48·9	3·12	152	140
0·038	0	48·9	3·12	152	140
0·0250	+	49·0	3·12	152	140
0·0225	?	48·5	3·125	150	138
0·0200	*u*	45·3	3·19	130	118
0·0175	*u*	40·2	3·27	108	96
0·0	*u*	−14·6	4·22	12	—

amount of coarse suspension. There appeared to be no appreciable change on increasing the concentration of potassium chloride to 1·0*M* for the *E.M.F.* determination. Only a minute trace of turbidity was produced on adding excess of potassium chloride to the clear and colourless supernatant liquid obtained with 0·020*M*-potassium chloride.

Experiment e.—Mixtures of sol J with a number of potassium and ammonium salts were prepared and investigated as described in Expt. *b*. The experiments were carried out, in duplicate, at a low room temperature. 0·239*N*-Sodium hydroxide was used to neutralise the bulk of the acid in every case. The results are given in Table VII, and plotted in Fig. 3.

TABLE VII.

Influence of anions on liberation of hydrogen ion (Sol J).

Salt.	Concentration.	Stability.	ΔE (mv.).	$a_H \times 10^4$.	Total acid.	Lib. H˙ ion.
KCl	0·500	0	130·6	195	0·168	0·026
	0·125	0	130·4	195	0·168	0·026
	0·133	0	129·2	186	0·166	0·024
	0·106	+	128·9	182	0·165	0·023
	Nil	*u*	111·5	89	0·142 †	—
K_2SO_4	0·500	0	103·8	68	0·168	0·026
	0·250	0	104·1	68	0·168	0·026
	0·120	0	102·7	65	0·166	0·024
	0·113	+	101·6	62	0·164	0·022
$(NH_4)_2SO_4$	3·0 *	*u*	81·5	27·5	0·152	(0·010)
	2·5 *	*u*	78·9	25·0	0·149	(0·007)
NH_4Cl	2·5	0	93·3	44	0·168	0·026
	2·0	0	93·1	44	0·168	0·026
	1·5	+ + (*u*)	95·4	47	0·166	0·024
	1·0	*u*	91·6	41	0·160	0·018
NH_4I	2·0	0	135·7	230	0·168	0·026
	1·5	0	135·4	230	0·168	0·026
	1·0	0	135·5	230	0·168	0·026
	0·75	+/0	134·1	220	0·166	0·024
	0·50	*u*	131·3	200	0·157	0·015
NH_4Cl	2·0 *	0	88·2	35·5	0·168	0·026

† No evaporation correction; filter entirely enclosed.

In calculating the values of total acid and liberated hydrogen ion, allowance was made for the evaporation during ultrafiltration, the filter being not entirely enclosed for these experiments; this amounted to 3·2% on the total acid. In the case of potassium chloride, the concentration of the salt in the cell solution was uniformly brought to 1·0*M*, and hence the value of a_H gave directly the concentration of unneutralised acid. To obtain the latter quantity in the case of another salt (with the exception of ammonium sulphate), the value of a_H was multiplied by the factor: (max. value a_H for KCl)/(max. value a_H for other salt). Since it proved impossible to attain a concentration of ammonium sulphate high enough to obtain the maximum value of a_H for this salt in the above manner, the following procedure was adopted. To 2·0 c.c. of the ultrafiltrate were added 1·0 c.c. of alkali and 2·0 c.c. of a solution containing ammonium chloride and ammonium sulphate of such strength that the final concentration of both salts was 3·0 equivs./l., and the value of a_H determined. The maximum value of a_H under the same conditions of measurement was obtained by starting from a mixture of sol and 2·0*M*-ammonium chloride (in which the ionic interchange was complete) and making up the cell solution by the addition, to the supernatant liquid, of alkali, ammonium chloride, and ammonium sulphate as just described. Thus in the case of ammonium sulphate (see expts. marked with an asterisk in Table VII), the concentration of unneutralised acid was given by

$$a_H[\text{max. } a_H \text{ for KCl/max. } a_H \text{ for } NH_4Cl + (NH_4)_2SO_4] = a_H(195/35{\cdot}5).$$

Since complete coagulation by ammonium sulphate was unattainable, comparison with other salts was made by means of the Zeiss nephelometer. The supernatant liquid from coagulation with 1·5*M*-ammonium sulphate at 13° gave a value of 0·220 for the absolute turbidity. A somewhat higher value, *viz.*, 0·248, was obtained with 0·0875*M*-potassium chloride under the same conditions. While, however, the concentration of liberated hydrogen ion in the case of potassium chloride was found by electrometric titration to be 0·022 equiv./l., that for the ammonium salt appeared to be only 0·013 equiv./l.

Experiment f.—Experiments of the same type as those described under Expt. *b* were performed with sol H, at 0°, 16°, and 50°. The results are recorded in Table VIII, and reproduced in Fig. 4. In the experiments marked by a double asterisk, the mixture was ultrafiltered at the appropriate temperature, and the bulk of the acid neutralised by 0·1015*N*-sodium hydroxide. A single asterisk denotes that 0·191*N*-alkali was employed. Neutralisation was effected with 0·267*N*-sodium hydroxide in every other case. The supernatant liquid or ultrafiltrate was allowed to attain room temperature before the definite volume (2 c.c. and 1 c.c. respectively) required for the acid determination was measured. The concentrations of potassium chloride which produced the degree of coagulation represented by " + " (see Expt. *b*) were found to be 0·063—0·075 at 0°, 0·122—0·138 at 16°, and 0·355—0·375 at 50°.

TABLE VIII.

Liberation of hydrogen ion in sol H at 0°, 16°, *and* 50°.

At 0°.				At 16°.				At 50°.			
Concn. KCl.	ΔE (mv.).	Total acid.	Lib. $H^{\cdot}$ $\times 10^3$.	Concn. KCl.	ΔE (mv.).	Total acid.	Lib. $H^{\cdot}$ $\times 10^3$.	Concn. KCl.	ΔE (mv.).	Total acid.	Lib. $H^{\cdot}$ $\times 10^3$.
1·5	110·8	0·156	39	1·5	114·2	0·160	36	1·5	117·2	0·162	32
1·0	104·4	0·150	33	1·0	112·4	0·157	33	1·0	118·7	0·163	33
0·5	105·4	0·151	34	0·5	112·5	0·158	34	0·4	117·7	0·163	33
0·25	104·3	0·150	33	0·25	111·9	0·156	32	0·375	139·5 *	0·163	33
0·075	103·6	0·150	33	0·125	136·3 *	0·156	32				
0·05	113·6 **	0·142	25	0·05	111·3**	0·133	9				

FIG. 3.

Sol J (Table VII).

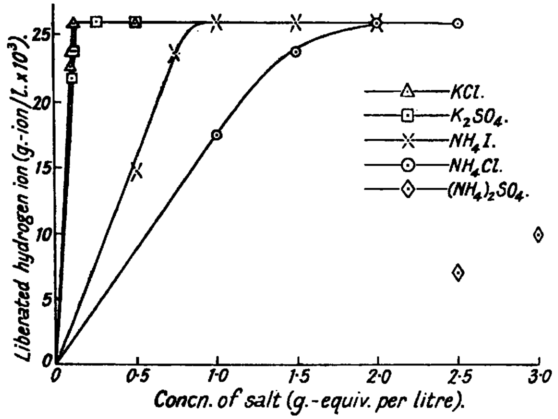
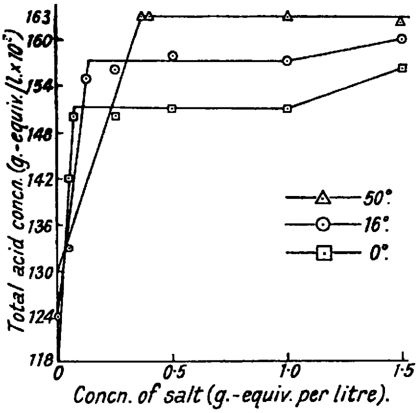


FIG. 4.

Sol H (Table VIII).



Experiment g.—A 10·0 c.c. sample of sol K was mixed with 5·0 c.c. of 0·501*N*-sulphuric acid, and the mixture kept at 0° or 16° for some hours. 2·0 C.c. portions were then completely coagulated with 2·0 c.c. of potassium chloride solution, and 2 c.c. of the supernatant liquid titrated (electrometrically) with 0·1041*N*-sodium hydroxide. The data obtained are shown in the following table.

TABLE IX.

Liberation of hydrogen ion by potassium chloride in the presence of sulphuric acid (Sol K).

	0°.		16°.	
Concn. KCl.	Titre (c.c.).	Total acid.	Titre (c.c.).	Total acid.
1·9	3·58	0·186	3·66	0·191
1·0	—	—	3·60	0·187
0·5	3·51	0·182	3·58	0·186

Experiment h.—A sol (L′) was prepared by mixing 50 c.c. of sol L with 4 c.c. of 4·25*N*-sulphuric acid. 10 C.c. of sol L′ were coagulated with 10 c.c. of 0·5*M*-potassium chloride. 10 C.c. of the clear supernatant liquid were evaporated to dryness, heated with concentrated sulphuric acid until fuming ceased, and then with ammonium carbonate (to convert pyrosulphate into sulphate). The weights of potassium sulphate obtained in duplicate estimations were 0·1946 and 0·1949 g. If no adsorption had occurred, the weight would have been 0·2179 g. The difference represents a decrease in concentration (*i.e.*, an adsorption) of 0·0266 equiv. of potassium per litre of sol–salt mixture.

By means of the glass electrode, it was ascertained that the amount of liberated hydrogen in the above mixture of sol L with potassium chloride was 0·029 equiv./l. The corresponding value for sol L′ was therefore = 0·029 × 50/54 = 0·0268 equiv./l.

2 C.c. of sol L′ were coagulated with 2·0 c.c. of 0·5*M*-potassium chloride. To 2 c.c. of the supernatant liquid were added 5·0 c.c. of 0·1040*N*-sodium hydroxide, and the unneutralised acid estimated by electrometric titration with the same alkali (titres, 1·40, 1·39 c.c.). The concentration of total acid in the supernatant liquid was thus found to be 0·332 equiv./l., as against 0·342, that in the whole system sol L + sulphuric acid.

10 C.c. of sol L were mixed with 10 c.c. of (*a*) 0·30*M*-potassium chloride in 2·13*M*-hydrochloric acid and (*b*) 0·30*M*-potassium chloride in 1·065*M*-sulphuric acid. Both mixtures were kept for some hours at 13°, ultrafiltered at the same temperature, and the potassium in 5 c.c. of ultrafiltrate estimated as potassium sulphate.

K_2SO_4, g.	(*a*) 0·0031, 0·0030 ;	(*b*) 0·0027, 0·0025
Adsorption of $K^{\cdot}$ ion (g.-ion/l.)	0·0070	0·0060

Finally the "bound" polythionic acid in sol L′ diluted with an equal volume of water was determined as silver sulphide (see Bolam and Muir, *loc. cit.*), 5 c.c. yielding 0·0334, 0·0340 g., whence the "bound" polythionic acid = 0·0270, 0·0275 equiv./l.

Experiment i.—Portions of sol G were diluted about two-fold and six-fold to give sols G_1 and G_2. In both cases sufficient hydrochloric acid was added to make the final concentration the same as in G. The following experiments were performed in duplicate. 2·0 C.c. of sol + 2·0 c.c. of 0·25*M*-potassium chloride, or water, were ultrafiltered (evaporation correction = 3·2%) and the value of a_H in 2·0 c.c. of ultrafiltrate + 1·0 c.c. of 0·478*N*-sodium hydroxide + 2·0 c.c. of water was determined by the glass electrode. It was found that the actual concentration of unneutralised acid was given by $1·27a_H$ in the presence, and $1·19a_H$ in the absence, of the potassium chloride. The results appear in Table X.

TABLE X.

Effect of sol concentration on liberation of hydrogen ion (Sols G, G_1, G_2).

Sol	G.	G_1.	G_2.
Concn. (g. S/100 c.c. sol)	9·83	4·46	1·91
Total acid (equiv./l.) in absence of KCl	0·254	0·254	0·254
„ „ „ presence „	0·287	0·272	0·262
Concn. liberated $H^{\cdot}$ ion (equiv./l.)	0·033	0·018	0·008
Micromols. $H^{\cdot}$ ion liberated from 1 g. of S ...	670	810	840

DISCUSSION.

Evidence that Ionic Interchange is of Primary Importance in the Coagulation Process.—It is difficult to avoid the conclusion that in the case of these sulphur sols the ionic interchange is directly involved in the coagulation process. Taking first the action of chlorides, it appears that, for a given sol at a given temperature, the amount of hydrogen ion liberated at any arbitrarily fixed "coagulation point" is a constant, *i.e.*, is independent of the nature (valency and lyotropic character) of the salt kation. In this connexion, the results of the measurements described in the present paper (Expt. *a*) amply confirm the data previously obtained. According to Table II, lithium chloride at a concentration of 3·51 equivs./l. produces an absolute turbidity of 0·250, which value we shall select for purposes of comparison. It may be deduced from the data for strontium chloride, given in the same table, that the corresponding concentration of this salt will be about 1% higher than 0·066 equiv./l., and that of potassium chloride about 1% lower than 0·10 equiv./l. The data in Table III show that the amounts (mean values) of hydrogen ion liberated by lithium at 3·51, potassium at 0·10, and strontium at 0·066 equiv./l. all lie within less than 4% of 0·026 equiv./l. This degree of variation is practically accounted for by the above-mentioned 1% divergences in the "coagulation values," together with the uncertainty of 0·01 c.c. in the titres (*i.e.*, 2% on the liberated hydrogen ion). It may therefore be concluded that at the given coagulation point and within the small experimental error, the same amount of hydrogen ion is liberated by the three salts, although the coagulation value of the lithium chloride is about 35 times as great as that of the potassium chloride, and over 50 times that of the strontium chloride. Liberation of the same amount of hydrogen ion, by the chlorides of potassium and ammonium under comparable conditions, is also indicated by the data in Table VII (Fig. 3). Summarising the results of the present and previous work, it can be said that equivalence in liberation of hydrogen ion at the coagulation point has been demonstrated for the following kations: lithium, sodium, potassium, rubidium, ammonium, calcium, barium, strontium, and aluminium.

As might be expected, in view of the behaviour of the very similar systems studied by Oden and others, the temperature exerts a considerable effect upon the coagulation (Expt. *b*); *e.g.*, the coagulation value of potassium chloride, in the case of sol K, decreases from 0·122 to 0·075 equiv./l. on lowering the temperature from 16·5° to about 0° (Table IV). No explanation has as yet been advanced to account for this peculiar influence of temperature, and it is therefore of great interest to find that here also there exists a close parallelism between the extent of coagulation and the degree to which hydrogen ion is liberated. Not only is it evident from the graphs in Fig. 1 that the lower the temperature the greater is the amount of hydrogen ion which appears in the intermicellar liquid, but the data also show that at the given coagulation point (denoted by "+"), the same proportion of hydrogen ion is liberated at the two temperatures.

The addition of ethyl alcohol (Expt. *c*) promotes the liberation of hydrogen ion, and simultaneously decreases the stability of the sol; *e.g.*, with sol J the presence of 40% of alcohol ($x = 100$) increases the actual liberation of hydrogen ion, by 0·3*M*-sodium chloride, from 62 to 100% of the potential. At the same time the coagulating action of the sodium chloride is so enhanced by the alcohol that practically complete coagulation is attained with 0·3*M*-salt (Table V), whereas in the absence of alcohol a concentration in the neighbourhood of 1·0*M* is required.

Several points of interest are raised by the results obtained with salts possessing different anions (Expt. *e*), the chief being the contrast between potassium chloride and sulphate, on the one hand, and ammonium chloride and iodide, on the other. While the replacement curves (Fig. 3) for the first pair of salts practically coincide, those for the second diverge markedly, the iodide showing the greater tendency to bring about replacement. This is in agreement with the present thesis, since the coagulation values (Table VII) of the potassium salts scarcely differ, whereas ammonium iodide is about twice as efficient a coagulant as ammonium chloride. Moreover, the amount of hydrogen ion liberated at the coagulation point ("+") lies, in all four cases, fairly close (within 5%) to the mean value of 0·023 equiv./l. A large part of the variation is probably due to experimental uncertainty, caused by the lack of strict temperature control, but another possible factor is the influence of the salt upon the effective acidity of the system (see below).

Ammonium sulphate presents a more complicated case than any so far discussed. While this salt at a concentration of 1·5*M* appears to liberate only about one-third of the available hydrogen in sol J (Table VII), the amount of coagulation, as roughly estimated by the appearance, indicated a much higher degree of replacement. The nephelometric measurements described in the last paragraph of Expt. *e* obviously confirm the existence of the apparent anomaly, which is undoubtedly to be attributed to adsorption of sulphuric acid by the micelles (see later). That the sulphate ion does, however, tend to diminish the actual ionic interchange is suggested by the experiments (Expt. *i*) in which sol L was treated with potassium chloride in the presence of hydrochloric acid on the one hand, and an equivalent concentration of sulphuric acid on the other. As the data show, the adsorption of potassium is distinctly less in the latter than in the former case. Reverting to the action of ammonium sulphate upon sol J, it would thus appear that, since the sulphate ion is present in very large amounts, the ionic interchange will be much reduced and the coagulation value correspondingly increased.

The influence of the remaining factor, acidity, is discussed at length in a previous communication (Bolam and Muir, *loc. cit.*), where it is shown that when acid (hydrochloric) is added to the sol, the coagulative action and replacing power of a salt are affected in parallel fashion. Attention is also directed to the fact that as the concentration of the acid is increased, the proportion of hydrogen liberated at the coagulation point is decreased. It is to be expected that the influence of the acid will be conditioned to a small extent by the nature and concentration of the added salt, since the salt may suppress the ionisation of the acid or diminish the activity of the hydrogen ions. As already suggested, this may be responsible for certain small variations in the degree of liberation of hydrogen ion at the coagulation point. Decrease in the concentration, or activity, of the hydrogen ions also probably accounts for the observation that complete coagulation of sol J containing 40% alcohol does not occur until the replacement rises to 100%.

It will be seen (Table I) that the quantity of hydrogen ion held by 1 g. of sulphur is a good deal higher in sol K than in sol J, although the concentration of sulphur in the former sol is somewhat less than in the latter. Apparently the conditions of preparation in the case of sol K were more favourable for the production of finely dispersed sulphur. The two sols contain almost identical amounts of hydrochloric acid, and yet the fraction of hydrogen ion liberated by potassium chloride at the coagulation point is 97% in the one case (K), as compared with 87% in the other (Tables IV and VII). A feasible explanation of the apparent discrepancy (of which several examples are to be noted throughout the work) is that the coagulation of the extremely fine (colourless) sulphur requires a higher concentration of salt in the case of sol K than in that of J, with the consequence that a greater amount of hydrogen ion is displaced from the coarser fractions of sulphur. In conformity with this view, we find that the respective " equilibrium " concentrations of potassium chloride are 0·092*M* for sol K, and 0·083*M* for J.

The Mechanism of Coagulation and the Interpretation of Variations in the Coagulation Value.—It may be taken as definitely established that in the case of the undialysed sols the disappearance of salt kations from the intermicellar liquid, and the accompanying increase in acidity of the last, is due solely to replacement of the hydrogen of the micellar polythionic acid by an equivalent amount of metal ion. This conclusion is based on the observed equivalence between " bound " polythionate and maximum adsorption of salt kation in sols F, F_2, F_3 (Bolam and Muir, *loc. cit.*), sol G (" *Sols* "), and sol L′ (Expt. *h*), and that between maximum adsorption of salt kation and maximum liberation of hydrogen ion in sols J (" *Sols,* " and Expt. *e*) and L′ (Expt. *h*). The data for sol L′ are particularly interesting, since a considerable amount of sulphuric acid had been taken up by the micelles in this case (see below). A further deduction from these results is that the whole of the polythionic acid must be accessible to the salt.

Of fundamental importance is the interpretation of the wide divergences in the replacing powers of the various kations. In view of these differences it is at least certain that more is involved than a simple exchange between the mobile hydrogen ions (" contra-ions " or " Gegenionen ") of the micellar polythionic acid and the salt kations. The suggestion was made in the first paper of the series that the principal complication is the formation of neutral molecules (or complexes) between a proportion of the replacing kations and the anions produced by the partial ionisation of the " bound " polythionic acid. According to this hypothesis, the interchange results in diminution of the actual *charge* on the sulphur surface. Moreover, application of the Donnan principle (cf. Gouy, *J. Physique*, 1910, **9**, 457; Chapman, *Phil. Mag.*, 1913, **25**, 475) leads to the conclusion that, since the liberation of hydrogen ion is the same for all salts at their respective coagulation concentrations, the extent to which the charge is suppressed is the same also. It thus appears reasonable to suppose that coagulation is brought about either by completely neutralising the charge, or by reducing it to some constant critical value.

Information on the last point is provided by the data for the dialysed sol J′ (Expt. *d*). This sol is comparable with the undialysed sols in that the liberated hydrogen is furnished solely by the micellar polythionic acid, although more than an equivalent amount of salt kation is taken up, the difference being due to adsorption of total salt (see Bolam and Bowden, *loc. cit.*). On the other hand, since the acidity of sol J′ is very low, the system is less complicated than in any other instance. It is therefore significant that complete coagulation of this sol is not attained until the whole of the hydrogen ion is liberated (Table VI), *i.e.*, until the charge is reduced to zero. That the same electrical condition is fulfilled in the case of more acid sols, where replacement at complete coagulation may be considerably less than 100%, is arguable on the basis of the present hypothesis. The high concentration of acid will itself produce a reduction in the charge, by suppressing the ionisation of the micellar polythionic acid, and a correspondingly smaller amount of polythionic salt need therefore be formed in order that the discharge should be complete.

So far no instance has been observed in which complete coagulation was not produced when the concentration of salt was sufficient to effect complete replacement. It is necessary to emphasise this, in view of some results recently published by Verwey and Kruyt (*loc. cit.*). These workers investigated the ionic interchange in negative silver iodide sols, stabilised by hydrogen iodide. They report that complete coagulation occurred at a concentration of the salt which was greater or less than that corresponding to complete liberation of the hydrogen ion, depending upon the nature of the salt, the concentration of the sol, and the extent of dialysis. Their conclusion is that the interchange has no connexion with the coagulation, except in certain very limited circumstances. A striking example of the behaviour observed is afforded by the case of a dilute sol in which all the hydrogen ion was liberated by a concentration of lead nitrate only 1/11 of that required for coagulation. Not even, however, in the case of the dilute sulphur sol J′, in which conditions would appear to be particularly suitable, is there any definite indication of the phenomenon. It is true that there is a little uncertainty in the concentration of potassium chloride necessary to bring about complete replacement; but even making the most unfavourable assumption, *viz.*, that it occurs at $0{\cdot}024M$ [where the extension of the initial inclined straight portion of the graph (Fig. 2) cuts the final flat portion], this is only 4% less than the coagulation value (Table VI), a scarcely significant difference.

As indicated above, the variation in the coagulation value amongst salts with the same anion but different kations may be ascribed to differences in the degree of ionisation, at the sulphur surface, of the respective polythionic salts or complexes. The influence of temperature and of the presence of alcohol may be equally well interpreted in similar fashion. If the surface dissociation decreases with fall in temperature (or on the addition of alcohol), the lower the temperature (or the higher the concentration of alcohol) the smaller will be the concentration of salt required to effect the degree of replacement necessary for coagulation.

It would seem that the replacing power, and therefore coagulative action, of a salt varies with the nature of the anion because of the tendency of this ion to decrease the concentration, or activity, of the kation. The effect increases with increase in the concentration of the salt, and will therefore be the more in evidence the weaker the specific replacing power of the kation. This accounts for the almost negligible difference between potassium chloride and sulphate on the one hand, and the marked difference between the iodide and chloride of ammonium on the other. Moreover, a bivalent anion exerts a greater interionic effect than does a univalent, which would explain why ammonium sulphate has a much higher coagulation value than the chloride or iodide. The same effect also appears to be responsible for the so-called "antagonistic" action of acids; *e.g.*, hydrochloric acid may be added to the sulphur sol in relatively large quantities without causing coagulation, and the high concentration of chloride ion reduces the effective concentration of the kation of the added salt to such an extent that its replacing action is very much reduced. While adsorption of the acid can undoubtedly occur, the results of the investigation afford no support for the idea that the sol is directly stabilised by such adsorption (cf. Dorfmann, *Kolloid-Z.*, 1930, **52**, 289).

The standpoint adopted throughout the investigation is essentially that advocated by Pauli (Pauli and Valkó, " Elektrochemie der Kolloide," Vienna, 1929), McBain (McBain and McClatchie, *J. Amer. Chem. Soc.*, 1933, **55**, 1315), Usher (*Trans. Faraday Soc.*, 1925—1926, **21**, 406), Pennycuick (J., 1929, 618), and Bassett and Durrant (*loc. cit.*). In opposition to this view, Verwey and Kruyt (*loc. cit.*) maintain that, in general, actual discharge of the micelles does not take place, but that coagulation results from compression (" Zusammendrückung ") of the diffuse electrical layer by the ions of the coagulant. Ionic interchange must inevitably occur, but plays no rôle in the coagulation process. Strongly polar (organic) ions are regarded as exceptional, in that they become fixed to (*i.e.*, are truly adsorbed by) the sulphur surface, and cause coagulation by neutralisation of the charge (" Entladung "). It has been shown in the present discussion that this is probably the normal behaviour of coagulating ions in the case of the sulphur sols examined, which raises the question as to how far these sols are comparable with those studied by Verwey and Kruyt.

Adsorption of Sulphuric Acid by Colloidal Sulphur.—It has already been shown (Expts. *g* and *h*) that sulphuric acid is adsorbed by the colloidal sulphur. Sol K was first diluted with one-half of its volume of sulphuric acid (0·0501*N*), and then again with an equal volume of salt solution. The total acid present will therefore be 0·200 equiv./l. As Table IX shows, however, the total amount of acid in the supernatant liquid from the completely coagulated sol varies from 0·182 to 0·191. Similarly in the case of sol L′, 0·332 equiv. appears in the supernatant liquid, as compared with 0·342 present in the whole system. Since the amount of potassium taken up by the coagulum in sol L′ is exactly equivalent to the " bound " polythionate, the liberation of polythionic hydrogen is evidently complete, so that the differences in question must be attributed to adsorption of sulphuric acid by the sulphur.

The experiments further reveal two interesting facts: (1) the adsorption increases with fall in temperature, (2) the hydrogen of the adsorbed acid is not replaced by other kations except at concentrations of salt far in excess of that which suffices to liberate the whole of the polythionic hydrogen. These characteristics of the adsorption make it possible to explain the apparently anomalous results obtained with sol H (Expt. *f*), on the assumption that this sol was not completely freed from the sulphuric acid used in its preparation. The different levels of the horizontal portions of the graphs in Fig. 4 may be interpreted as due to decrease in the adsorption of the acid as the temperature rises, and the inflexions at high salt concentrations to replacement of the hydrogen of the adsorbed acid. Now the total acid in the intermicellar liquid of the mixture sol H + water was found, by ultrafiltration, to be 0·124 equiv./l. at 16°, so the available micellar polythionic hydrogen amounted to 0·033 equiv. Assuming that the same value holds at the other temperatures, we may deduce the values for liberated hydrogen given in Table VIII. The maximum liberated hydrogen in the very similar sol K is 0·031 (Table IV), and if the values for sol H (with the exception of those at very high salt concentrations) are multiplied by the factor 31/33, the points obtained lie very close to the graphs in Fig. 1. The two sols thus behave almost identically with regard to temperature and salt concentration.

Influence of Concentration of Sol on the Ionic Interchange.—In order to evaluate the effect of diluting sol G (Expt. *i*) upon the degree of replacement, it is necessary to apply a simple calculation to the data in the last line of Table X. The values given for liberated hydrogen ion are not strictly comparable since the same amount of potassium chloride was added in every case, so that the final, or equilibrium concentration of the salt in the intermicellar liquid is the smaller the more concentrated the sol. As, however, in the case of potassium chloride over the range of concentration concerned, the replacement is directly proportional to the equilibrium concentration, it is a simple matter to deduce the replacement for a given value of the latter. Actually, for an equilibrium concentration of 0·125M, the liberated hydrogen works out at 910 micromols. per g. of sulphur in sol G, 940 in G_1, and 910 in G_2, *i.e.*, is practically the same in all three cases.

Achar and Usher (J., 1927, 1875) find that the amount of hydrogen liberated from a given quantity of finely dispersed stearic acid by a fixed concentration of potassium sulphate increases with dilution of the suspension. This is traced to the influence of the ratio between the volume of external salt solution and that of the diffuse ionic surface layers of the particles on the extent to which the surface acid is ionised. It is also shown that the effect is qualitatively in agreement with the Donnan theory. On this view, constancy in the degree of replacement with increasing dilution of the suspension indicates (1) that the replacement is complete, or (2) that the tendency of the surface molecules to ionise does not vary. Since in the case of the sulphur sols the replacement is incomplete, it would appear that the high concentration of acid, present in all three systems, prevents any appreciable change in the ionisation of the micellar polythionic acid, when the sulphur content of the sol is reduced.

Ultrafiltration.—It is evident that the validity of many of the foregoing conclusions depends upon the reliability of the results obtained with ultrafiltrates. McBain and McClatchie (*loc. cit.*; see also McBain, Kawakami, and Lucas, *J. Amer. Chem. Soc.*, 1933, **55**, 2762) have shown that the acidity of the ultrafiltrate from a well-dialysed " ferric hydroxide " sol is very much influenced by the speed of the filtration. At low rates, such as were employed in the present investigation, the acidity rises rapidly with decrease in the rate. This is ascribed to the establishment of a Donnan equilibrium across the filtering membrane; *a priori* it is improbable that correction for this effect is necessary in the case of the undialysed sulphur sols, since a high concentration of acid is always present, and in most cases a large amount of salt as well. The good agreement in the estimations of liberated hydrogen ion, adsorbed salt kation, and micellar polythionic acid supports this contention. The effect will, of course, be most pronounced in the ultrafiltration of the system obtained by diluting the dialysed sol J′ with water, where the figure given for total acid (Table VI) may be too high. However, even if the error here is very large, the conclusions drawn regarding sol J′ would, as a whole, be unaffected.

SUMMARY.

1. The influence of the following factors upon the ionic interchange in sulphur sols has been investigated: (1) nature of salt kation, (2) temperature, (3) presence of alcohol, (4) nature of salt anion, (5) acidity, (6) sol concentration. The dependence of the coagulation values of salts upon these factors (except the last) has also been examined.

2. It is found that a close relationship always exists between the coagulative action of a salt and the replacing capacity of the kation under the given conditions. The conclusion is drawn that the ionic interchange is an essential part of the coagulation mechanism.

3. It is shown that the coagulation may be reasonably regarded as due to diminution of the actual charge on the sulphur surface by the formation of unionised molecules, or complexes, between the coagulating kations and the micellar polythionic anions. The effect of any given factor on the coagulation value is interpreted in terms of (1) variation in the specific ionising tendency of the surface molecules, or complexes, and (2) variation in the concentration, or activity, of the coagulating ions.

4. Adsorption of sulphuric acid by the colloidal sulphur is shown to occur, but no evidence has been found that such adsorption is a stabilising factor.

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