240. *Ionic Interchange in Sulphur Sols. Part II. The Influence of Acids.*

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The results of an investigation of ionic interchange in well-dialysed Raffo sulphur sols stabilised by a polythionic acid (Bolam and Bowden, J., 1932, 2864) indicated that when the concentration of sulphur was 3% and the total concentration of acid of the order $0{\cdot}01M$, the sol became practically completely coagulated at the concentration of salt which just sufficed to liberate the whole of the hydrogen ion from the sulphur micelles. Some preliminary experiments appeared to show that the liberation of hydrogen ion was incomplete at the coagulation point when the sol was concentrated by evaporation, and it was suggested that this behaviour might be due to adsorption of hydrogen chloride (the coagulating salts being chlorides) as a consequence of the increased acidity (0·05*M*). This view appeared reasonable in so far that the existence of adsorption of chloride by the micelles was found to occur.

A study has now been made of ionic interchange in sols of the same nature as the above, but undialysed and containing greater amounts of acid. With these sols, total coagulation occurred before the whole of the hydrogen ion was liberated, and it was established that the actual kationic interchange was incomplete. The degree of replacement at the coagulation point decreased with increase in the concentration of acid, but its value proved to be independent of the nature of the kation of the coagulating salt, in confirmation of the previous work. It was further established that increase in the concentration of acid not only decreased the amount of hydrogen ion liberated at the coagulation point, but also increased the concentration of salt necessary to secure this amount of replacement. The former of these effects appears to be connected with the coagulating action of the acid, and the latter with its so-called " antagonistic " action.

EXPERIMENTAL.

Sols.—A solution of 84 g. of sodium thiosulphate in 50 c.c. of water was slowly added to 65·5 c.c. of concentrated sulphuric acid with constant stirring, the temperature being kept below 25°. The sulphur was coagulated with 100 c.c. of 4*M*-sodium chloride, separated on a Buchner funnel, and repeptised in 100 c.c. of water by warming to 80°. After a second coagulation with sodium chloride, the sulphur was twice coagulated with concentrated hydrochloric acid. In order to obtain a sufficiently concentrated sol, several lots of sulphur were prepared in the above fashion, and peptised together in 100 c.c. of water. The sol was clarified by centrifuging for 15 min. at 9,000 r.p.m. No attempt was made to remove hydrogen chloride except by allowing the final coagulate to drain thoroughly. Flame tests showed that the sodium content of the sols was negligible. The concentration of the sol was determined as described by Bolam and Bowden (*loc. cit.*).

A.R. Salts (with the exception of rubidium chloride) and acids, " pure " sodium hydroxide, and water of $\kappa = 1{\cdot}25 \times 10^{-6}$ mho, were employed throughout the research.

Liberation of Hydrogen Ion.—The degree of liberation of hydrogen ion at the coagulation point was determined for various salts as follows. 2 C.c. of sol were shaken for 3 min. with 2 c.c. of salt solution of known concentration in a glass-stoppered tube, and the mixture examined after standing for about 18 hours, by which time the supernatant liquid was clear and either colourless or still yellow. It was found that the liquid might be colourless although a small quantity of sulphur remained uncoagulated, and the coagulation value of the salt was therefore taken as that concentration which just sufficed to give a supernatant liquid showing only a trace of turbidity on the addition of large excess of the salt.

The further procedure is best elucidated by taking a concrete case. 2 C.c. of sol D + 2 c.c. 2*M*-potassium chloride gave a colourless supernatant liquid. 2 C.c. of this were mixed with 1 c.c. of 0·08*N*-sodium hydroxide (to neutralise the bulk of the acid) and 2 c.c. of 1·5*M*-potassium chloride, so that the final concentration of the latter salt was 1·0*M*. The concentration of unneutralised acid in the mixture was determined potentiometrically by means of cells of the type

$$\begin{array}{l|l|l|l|l|l|l}
\mathrm{Hg} & \mathrm{Hg_2Cl_2,\ KCl} & \mathrm{KCl} & x & \text{Glass} & \mathrm{HCl,\ \ Quinhydrone} & \mathrm{Pt} \\
 & \text{(solid)}\ \ 3{\cdot}5M & 3{\cdot}5M & & \text{membrane} & 0{\cdot}1M\ \ \ \ \text{(solid)} & \text{(polished)}
\end{array}$$

(cf. Morton, *J. Sci. Instr.*, 1930, **1**, 187). Let E = e.m.f. with 0·05*M*-potassium hydrogen phthalate ($p_H = 3{\cdot}97$) as electrode solution (x) and E' = e.m.f. with above mixture; then $\Delta E = E - E' = 0{\cdot}1075$ v., $p_H = (3{\cdot}97 - \Delta E/0{\cdot}0577) = 2{\cdot}11$, and $a_H = 0{\cdot}078$. Experiment showed that on the assumption that the acid was hydrochloric, the concentration was equal in value to a_H under the given conditions. Hence the total concentration of acid in the mixture was $0{\cdot}08/5 + 0{\cdot}0078 = 0{\cdot}0238N$.

The proportion of acid which was already present in the intermicellar liquid before the addition of the salt was found by ultra-filtering 2 c.c. of sol + 2 c.c. of water and determining ΔE for the mixture 2 c.c. ultrafiltrate + 1 c.c. 0·08N-sodium hydroxide + 2 c.c. of 2·5M-potassium chloride (to make the final concentration of the last again 1·0M). The figures obtained were ΔE = 0·0116 v., p_H = 4·17, $[H^{\cdot}] = a_H$ = 0·0001, so that total concentration of acid was 0·08/5 + 0·0001 = 0·0161N. Ultrafiltration was carried out by the method of Bolam and Bowden (*loc. cit.*), the evaporation correction being reduced to 3·2% by improved shielding. Hence, applying the evaporation correction, the true concentration of acid derived solely from the intermicellar liquid of the original sol was 0·0161 × 0·968 = 0·0155N, and that of the hydrogen ions replaced in the micelles by potassium = 0·0238 − 0·0155 = 0·0083 g.-ion per litre.

The glass electrode was constructed as described by MacInnes and Dole [*Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 57; *J. Amer. Chem. Soc.*, 1930, **52**, 29], the membrane being made from glass of the formula recommended by Morton (see Harrison, J., 1930, 1528) and supplied by C. Dixon and Co., London. The calomel electrode was made according to the design of Greville and Maclagan (*Trans. Faraday Soc.*, 1931, **27**, 219). The cell was set up in an air thermostat maintained at 18° ± 0·5° by electrical regulation. A circuit of the type introduced by Morton (J., 1931, 2978) was employed, the essential components being a G.E.C. triode valve, a Tinsley " Ionisation " potentiometer, and a Gambrell " High Sensitivity " galvanometer. Null-point determinations were invariably certain to within 0·2 mv., and generally 0·1 mv.

FIG. 1.

Sol D (*Table I*).

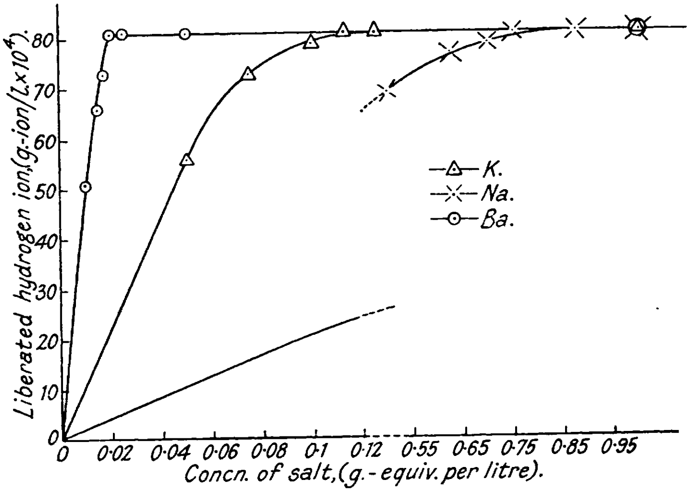


Table I contains the data. Col. 2 gives the concentration of salt (in g.-equiv. per litre) in the initial mixture of 2 c.c. sol + 2 c.c. salt solution, to which the stability observations refer. In col. 3 *u* denotes that the supernatant liquid was yellow (in which case the mixture was ultra-filtered and the liberated hydrogen ion determined from the ultrafiltrate). The other symbols imply that this liquid was colourless and indicate the degree of turbidity produced by the addition of excess of salt. Thus 0 = none, + = trace, ++ = moderate, and +++ = marked.

In every case the value of ΔE (col. 4) is the mean of two quite independent determinations, which generally agreed to within 0·6 mv. and in no instance differed by more than 1·2 mv. By the addition of 2 c.c. of salt solution of suitable concentration to the mixture of 2 c.c. of supernatant liquid + 1 c.c. of alkali, the values of a_H were determined at a constant salt concentration, the value of which, in mols. per litre, is given in parentheses in col. 1. Variations in a_H were thus due solely to differences in the amount of liberated hydrogen ion. The concentration of unneutralised acid in the case of salts other than potassium chloride was obtained by multiplying the appropriate value of a_H by the factor (maximum $a_H)_{KCl}$/(maximum $a_H)_{\text{other salt}}$.

The last column of the tables shows the concentration of liberated hydrogen ion (expressed as g.-ion per litre × 10^4) after diluting 2 c.c. of supernatant liquid (or ultrafiltrate) to 5 c.c. (see above). It is estimated that the values are correct within 2%. The results are plotted in Figs. 1 and 2, and the percentage replacement, given in the last column of Table III, obtained from the graphs by reading off the liberated hydrogen ion corresponding to the coagulation value as deduced from Tables I and II.

TABLE I.

Liberation of hydrogen ion in Sol D.

Salt, and concn.		Stability.	ΔE (mv.).	p_H.	$a_H \times 10^4$.	Liberated $H^{\cdot}$ ion.	Salt. and concn.		Stability.	ΔE (mv.).	p_H.	$a_H \times 10^4$.	Liberated $H^{\cdot}$ ion.
KCl	1·000	0	107·5	2·11	78	83		0·750	0	106·8	2·12	76	81
	0·125	0	106·8	2·12	76	81		0·700	0	106·1	2·13	74	79
(1·0)	0·113	0	106·9	2·12	76	81		0·625	++	105·4	2·14	72	77
	0·100	0	106·2	2·13	74	79		0·500	*u*	105·2	2·15	71	69
	0·075	+	104·1	2·17	68	73	$BaCl_2$	1·000	0	112·7	2·02	96	80
	0·050	*u*	100·2	2·23	58	56		0·050	0	112·8	2·02	96	80
NaCl	1·500	0	107·3	2·11	77	82	(0·4)	0·025	0	113·2	2·01	98	82
	1·250	0	107·0	2·12	77	82		0·020	0	113·4	2·01	99	83
(1·5)	1·000	0	107·1	2·11	77	82		0·0175	+	110·4	2·06	88	73
	0·875	0	106·1	2·13	74	79		0·015	+++	107·6	2·11	79	66
								0·010	*u*	104·0	2·17	68	51

*Liberation of hydrogen ion in Sol E.**

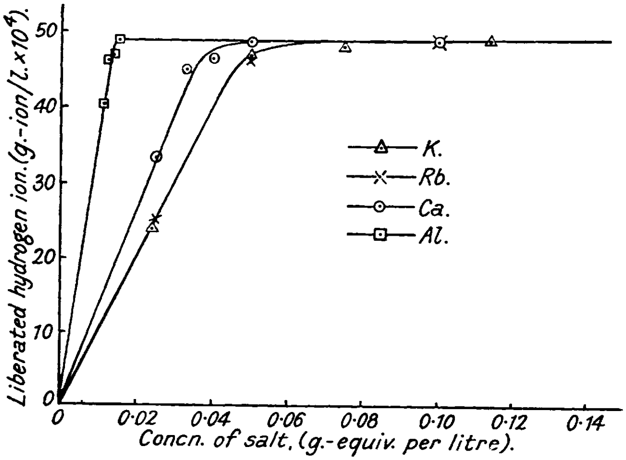
Salt, and concn.		Stability.	ΔE (mv.).	p_H.	$a_H \times 10^4$.	Liberated $H^{\cdot}$ ion.	Salt. and concn.		Stability.	ΔE (mv.).	p_H.	$a_H \times 10^4$.	Liberated $H^{\cdot}$ ion.
KCl	0·500	0	76·5	2·64	23	49	$CaCl_2$	1·000	0	82·3	2·55	28	49
	0·113	0	76·7	2·64	23	49		0·100	0	82·1	2·55	28	49
(1·0)	0·100	0	76·8	2·64	23	49	(1·0)	0·050	0	82·4	2·54	29	50
	0·075	0	76·0	2·65	22	48		0·040	+	79·2	2·60	25	46
	0·050	0	74·5	2·68	21	47		0·033	+++	77·8	2·62	24	45
	0·048	++	—	—	—	—		0·025	*u*	69·3	2·77	17	33
	0·024	*u*	31·3	3·43	4	24	$AlCl_3$	1·500	0	34·7	3·37	4·3	49
RbCl	0·500	0	80·1	2·58	26	49		0·0150	0	34·0	3·38	4·2	49
	0·200	0	79·9	2·58	26	49	(0·4)	0·0135	0	32·4	3·41	3·9	47
(0·2)	0·100	0	80·4	2·58	26	49		0·0120	++	32·0	3·42	3·8	47
	0·050	0	77·0	2·64	23	46		0·0113	*u*	32·9	3·40	4·0	41
	0·048	++	—	—	—	—							
	0·025	*u*	37·6	3·32	5	25							

* Concentration of acid derived from intermicellar liquid of original sol = 0·0165*N*. Concentration of alkali used for neutralisation = 0·0956*N*.

Adsorption of Barium Ion.—The adsorption of barium ion just above the coagulation point was determined as illustrated by the following example. 2 C.c. of the supernatant liquid from 2 c.c. of sol + 2 c.c. of 0·1*M*-barium chloride were evaporated to dryness and heated to 130° for 3—4 hours to remove hydrogen chloride. 10 C.c. of water were added to the residue, and the conductivity measured at 25° ± 0·05° by the usual method. The concentration of barium chloride was derived from the conductivity (corrected for non-volatile constituents of the sol) by means

FIG. 2.

Sol E (Table I).



of a graph plotted from data given in the International Critical Tables (Vol. VI, p. 233) and found to be $18{\cdot}45 \times 10^{-5}$ g.-equiv. per 10 c.c. If no adsorption had taken place the concentration would have been $0{\cdot}1 \times 2/1000 = 20{\cdot}00 \times 10^{-5}$ g.-equiv. per 10 c.c. Hence the amount of barium ion adsorbed by the sulphur in 1 c.c. of sol was 0·0000155 g.-equiv.

The following table contains the results; c is the concentration of barium chloride (in g.-equiv. per litre) in the initial mixture of sol and salt solution. The remaining figures are the amounts of barium ion, expressed as g.-equiv. × 10^7, adsorbed by the sulphur in 1 c.c. of sol. It is estimated that the adsorption values given are correct to within about 2%.

Adsorption of barium ion.

c	0·161	0·100	0·025	0·020	0·0175	0·0125	0·01125	0·0090	0·0085
F	—	155	159	—	—	—	—	153	147
F_1	—	—	149	—	—	151	141		
F_2	—	151	152	146	138				
F_3	124								

Sols F_1 and F_2 were prepared by mixing approx. 50 c.c. of sol F with about 2 c.c. of hydrochloric acid of suitable concentration, and sol F_3 by mixing the unused portions of F_1 and F_2. In the case of sol F_3 the procedure was slightly different, in that the coagulation was carried out with barium chloride solutions containing a constant large amount of hydrogen chloride, so that the final concentration of acid in the sol + salt mixture was *ca.* 2·2M.

The lowest concentration of salt at which the adsorbed barium ion was determined was, in each case, definitely above the coagulation value. A concentration of salt which just failed to produce coagulation was also found, and the corresponding value of the adsorbed barium ion obtained from a graph plotted from the appropriate data in the above table.

Estimation of Polythionic Acid.—The amount of polythionic acid " bound " by the sulphur micelles was estimated by a method resembling that used by Bassett and Durrant (J., 1931, 2946). 5 or 10 C.c. of sol were completely coagulated with potassium chloride, the coagulum filtered off and well washed with potassium chloride solution, the small filter-paper pierced, and the sulphur washed into a beaker by the aid of 50 c.c. of water. After heating to boiling, 5 c.c. of nitric acid of suitable concentration (see Bassett and Durrant, *loc. cit.*) and slight excess of silver nitrate were added, and the mixture kept at 100° for 10 mins., to convert the polythionate into silver sulphide. The precipitate was filtered off, washed with cold water, treated with cold dilute ammonia to dissolve out silver chloride, and gently ignited, apart from the filter-paper, in a very small crucible. The amount of silver sulphide adhering to the paper was found by burning the latter and weighing the silver residue. Table II shows the results of the analyses. In col. 4 is given the amount of polythionate (calculated from the weight of silver sulphide) held by the sulphur on 1 c.c. of sol, and in col. 5, the maximum amount of barium adsorbed, as determined by the conductivity method. It will be seen that for a given sol these quantities are equal, so that the adsorption of barium ion must have taken place only by interchange with the polythionic $H^{\bullet}$ and not as the result of adsorption of Cl'. Hence the values for $Ba^{\bullet\bullet}$ adsorption given in Table II also represent $H^{\bullet}$ liberation and the limiting percentage values of the latter at the coagulation point may be calculated. These are given in Table III.

TABLE II.

Equivalence between micellar polythionate and maximum adsorption of barium.

Sol.	C.c.	Ag_2S (g.).	Polythionate (g.-equiv. × 10^7).	Ba (g.-equiv. × 10^7).	Sol.	C.c.	Ag_2S (g.).	Polythionate (g.-equiv. × 10^7).	Ba (g.-equiv. × 10^7).
F	5	0·0099	160	157	F_3	10	0·0186	150	148
	5	0·0100				10	0·0189		
F_2	10	0·0197	159	152					

CONCLUSIONS.

Equivalence of Interchange at the Coagulation Point.—The first important feature of the results is that within the experimental error (probably not more than 3%) the same fraction of hydrogen ion is liberated at the coagulation point, in the case of a given sol, whatever the nature of the kation of the coagulating salt. This is clearly shown by the figures for sols D and E given in the last column of Table III. It thus appears, as was indicated by the observations of Bolam and Bowden (*loc. cit.*), that in the case of these sulphur sols the coagulating efficiency of any particular kation corresponds closely to its tendency to displace hydrogen ion from the surface of the micelles. The differences between the coagulation values of the various salts must therefore ultimately depend upon the manner in which the ionic interchange is influenced by the valency, hydration, and other properties of the coagulating ions.

TABLE III.

Degree of ionic interchange at the coagulation point.

Sol.	[HCl].	Salt.	Coagulation value.	H˙ liberated, %.
E	0·053	KCl	0·049	95
		RbCl	0·049	95
		$CaCl_2$	0·040	97
		$AlCl_3$	0·0128	95
D	0·060	KCl	0·075	89
		NaCl	0·663	95
		$BaCl_2$	0·0175	92
F	0·060	$BaCl_2$	0·008—0·0085	88—93
F_1	*ca.* 0·100	,,	0·010—0·0125	88—93
F_2	*ca.* 0·250	,,	0·015—0·0175	80—91
F_3	*ca.* 2·200	,,	0·140—0·161	75—84

Weiser and Gray (*J. Physical Chem.*, 1932, **36**, 2796) report that the displacement of hydrogen ion from the micelles in a sol of arsenious sulphide is completed at a concentration of salt definitely below the coagulation value. No instance of this phenomenon has so far been observed in the present studies on sulphur sols.

Influence of Acid upon the Degree of Interchange at the Coagulation Point.—From a consideration of the figures as a whole, it is evident that the degree of liberation of hydrogen ion at the coagulation point decreases as the total acidity increases ([HCl] = molar concentration of acid in the initial mixture of sol and salt). As the adsorption of barium shows, the unliberated hydrogen must be present in the coagulated micelles as polythionic acid, so that the kationic interchange is actually incomplete, and the effect is not due to adsorption of hydrogen chloride. It would appear that total interchange at the coagulation point can occur only in the complete absence of acid, but the work of Bolam and Bowden (*loc. cit.*) shows that for all practical purposes the condition is reached at an acid concentration of 0·01*M*.

At the highest concentrations, the acid itself coagulated some of the coarser sulphur, a definite turbidity being produced by 0·25*M* and a considerably greater effect by 2·2*M*. According to the view advanced in the previous paper, coagulation by an acid is due to the formation of un-ionised polythionic acid in the micelles, owing to the suppression of the ionisation by the added hydrogen ions. It may therefore be supposed that the tendency to form un-ionised polythionic acid accounts for the decrease in the amount of interchange at the coagulation point with increase in acidity, since less metal polythionate need be formed in order that the whole of the micellar polythionate may be present as un-ionised molecules of some kind, which is the postulated condition for coagulation. Now, a very high concentration of acid (about 7·0*M* in the case of sol *F*) is required to coagulate the finest particles, which means that the tendency to form un-ionised polythionic acid falls off rapidly with decrease in particle size. It follows that the degree of interchange necessary for the coagulation of all the sulphur should change slowly relative to increase in the concentration of acid. The data in Table III show that this actually happens, for, taking the extreme case, it will be seen that while the acidity increases from 0·05*M* to 2·2*M*, *i.e.*, 44-fold, the fraction of hydrogen remaining in the coagulum increases from 4 to 20%, or only 5-fold. Decrease in the tendency to form un-ionised polythionate with diminution in micellar dimensions would also explain the shape of the replacement curves, since, as suggested in the previous communication, the amount of replacement depends upon the tendency of the in-going kation to form un-ionised polythionate.

Sol *D* contained 8·13 g. of sulphur per 100 c.c. of sol, Sol *F* 4·65 g., and Sol *E* some intermediate quantity. The sols thus differed considerably in concentration, but it is evident that any influence of this factor upon the interchange at the coagulation point was of secondary importance in the present series of experiments. The question of the relationship between sol concentration and degree of interchange is being more closely examined.

The " Antagonistic " Action of Acids.—The data for the coagulation of Sols *F*, etc., by barium chloride show that while the adsorption of barium at the coagulation point slowly decreases as the concentration of acid increases, the concentration of salt necessary for the production of a given degree of adsorption increases in a very marked fashion. It is evident that the so-called " antagonism " of the acid, *i.e.*, its power of opposing coagulation by a salt, is the consequence of the decrease in the tendency to ionic interchange which the acid produces.

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