402. *Ionic Interchange in Sulphur Sols. The Lyotropic Series and the Mechanism of Coagulation.*

By Thomas R. Bolam and George Bowden.

A survey of the data for the coagulation of inorganic sols by electrolytes shows that the occurrence of the lyotropic sequence of the alkali-metal kations, first clearly established by Pappadà (*Gazzetta*, 1903, **33**, [ii], 272), is quite general, being confined to no particular type of sol. No satisfactory interpretation of the phenomenon has yet been advanced, and further correlation between the coagulating action of these ions and other effects produced by them in the colloidal system is necessary. The following experiments were designed to ascertain if any definite relationship could be found between the extent of adsorption of the ions by the colloidal particles and the corresponding influence on the stability of the sol.

According to current conceptions, a negative sol owes its stability to the fixation of negative ions on the surface of the particles, which attract an equivalent amount of positive ions to form an outer layer or sheath. When a salt is added to the sol, adsorption of the kation may take place in a double fashion : (i) kations of the added salt may replace those of the stabilising electrolyte (" ionic interchange " or " base-exchange ") ; (ii) anions of the added salt may become attached to the surface of the particles, taking with them an equivalent amount of kation (" adsorption of total salt "). The present investigation deals primarily with ionic interchange in Odén sulphur sols stabilised by a polythionic acid (replaceable ion = $H^{\cdot}$). Adsorption of total salt is shown to exist, but under the given conditions, this appears to introduce practically no complications.

These sulphur sols provide particularly suitable material for our purpose : (1) they may be prepared with a large active surface of sulphur, so that adsorption measurements are reasonably accurate ; (2) as has been shown by Odén (*Nova Acta Upsala*, 1913, iv, **3**, 156), Freundlich and Scholz (*Koll.-Chem. Beih.*, 1922, **16**, 234), Weiser and Cunningham ("Colloid Symp. Monograph," 1928, **6**, 319), Dorfman (*Kolloid-Z.*, 1928, **46**, 186), and Bassett and Durrant (J., 1931, 2946), their lyotropic effect is very pronounced; (3) according to the last authors, there is no tendency for the anion of the added salt to replace the stabilising anion at the surface of the sulphur.

EXPERIMENTAL.

Preparation and Characteristics of Sols.—Colloidal S was obtained by the interaction of $Na_2S_2O_3$ with H_2SO_4. In order to favour the formation of peptisable S, only small quantities of the reactants were employed in each operation, the following procedure being uniformly adopted. 25 C.c. of conc. H_2SO_4 were slowly run into 100 c.c. of sat. $Na_2S_2O_3$ aq., the mixture being vigorously stirred and maintained at 30°. Immediately after the addition of the acid, the mixture was cooled in ice and 100 c.c. of sat. NaCl aq. added. The resulting coagulum was collected by means of the centrifuge, and heated to 80° with 100 c.c. of H_2O. Coagulation and redispersion were then repeated until the supernatant liquid after coagulation was neutral to litmus. The final dispersion was freed from coarse S by centrifuging for ½ hr. at 9000 r.p.m.

Sufficient material for a complete series of experiments having been thus prep., the whole was mixed and freed from NaCl by repeated coagulation with conc. HCl. The sol was then dialysed for 6 weeks in collodion bags suspended in running water, and finally stored in the dark in a Jena-glass bottle.

The sols were free from salts, since they imparted no colour to the flame and yielded the merest trace of residue on evaporation and gentle ignition. On the other hand, they contained appreciable amounts of acid, the bulk of which was associated with the S particles. No attempt was made to ascertain by direct analytical means the proportion of HCl present, but we have good reason to regard it as negligible. No adsorption of added HCl by the S could be detected when the acid was present in $0{\cdot}01M$-concn., though considerable adsorption was observed at $0{\cdot}05M$ (cf. Rindé, *Phil. Mag.*, 1926, **1**, 44). Since the acidity of the intermicellar liquid of the sol itself was always much less than $0{\cdot}01M$ (Table I), it follows that the adsorbed acid was some other than HCl. In the light of the researches of Freundlich and Scholz and of Bassett and Durrant (*loc. cit.*), it appears certain that the only electrolytes retained by the sols after dialysis consisted of pentathionic and, probably, hexathionic acid.

During dialysis, considerable quantities of coarse cryst. S were deposited by the sols, but filtration of the end-product gave clear sols in which any tendency to spontaneous change was of minor importance.

The S content of the sols was determined as follows. A weighed portion of sol was placed in an open crucible on the steam-bath for 30 mins., and then kept at 120° in an air-oven until the S melted, the latter operation being repeated till constant weight was attained. Loss of S was negligible under these conditions.

Table I shows that the three sols employed in the present investigation were comparable.

Reagents.—With the exception of the Li salts, A.R. reagents were used throughout. Two samples of LiCl were employed, the one as purchased, the other after purification; these gave identical results. All solutions were made up with H_2O of $\kappa = 1{\cdot}1 \times 10^{-6}$ mho, and stored in Jena-glass bottles. The concns. of the chloride solutions used in the determination of total salt

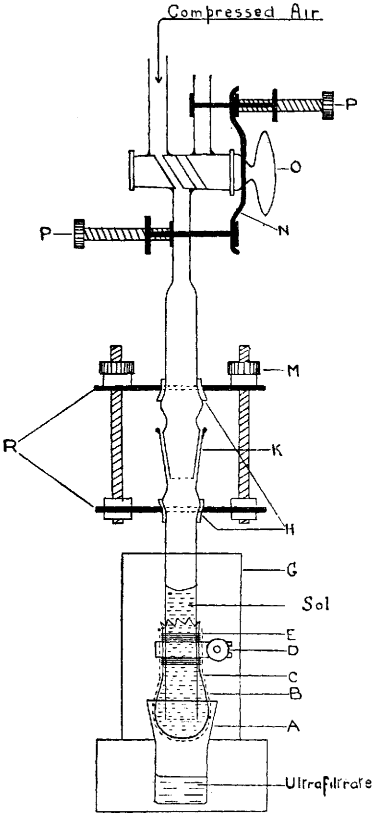
TABLE I.

Sol.	S, g./100 c.c. sol.	After dilution with equal vol. of H_2O, [H$^{\cdot}$] in intermicellar liquid.	 Micromols. of adsorbed H$^{\cdot}$ per g. S.
A	3·146	0·00145	612
B	3·292	0·00075	407
C*	3·830	0·00043	555

* Sol C was concentrated to approx. the same strength as Sols A and B by evaporation at 50°.

adsorption were checked by means of conductivity measurements, use being made of appropriate data from the International Critical Tables (VI, 236).

FIG. 1.

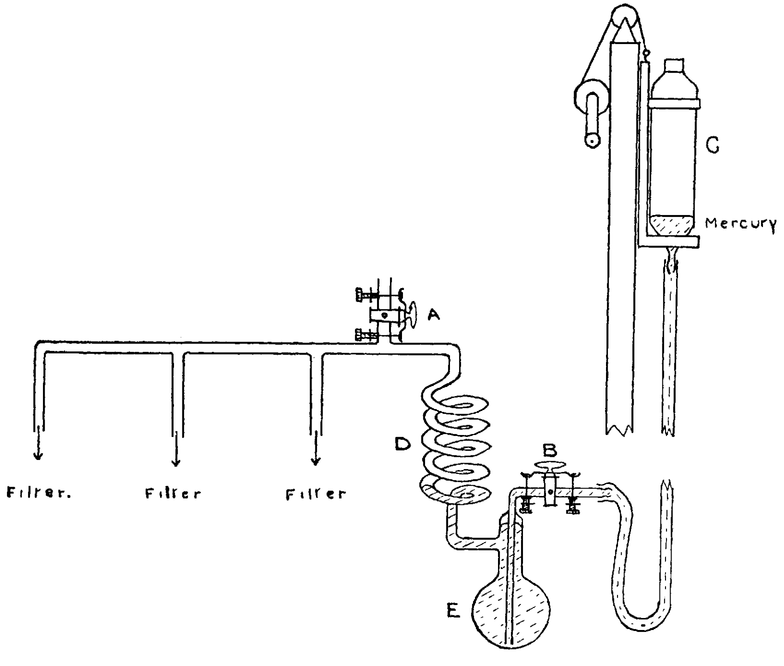


Determination of Liberated Hydrogen Ion.—The procedure consisted in (1) the mixing of equal vols. of sol and salt solution of known comp., (2) the ultrafiltration of the mixture, and (3) the determination of the acid content of the ultrafiltrate by means of the quinhydrone electrode. Where total coagulation occurred and the S settled rapidly, the *E.M.F.* measurement was carried out with the supernatant liquid. In order to economise the sols, only *ca.* 2 c.c. were used for each experiment, being measured by a pipette. The constancy in delivery of the latter was carefully checked, and the vol. was always within 1·5% of a mean value of 2·017 c.c.

An ultrafilter was devised to deal with the small quantities of liquid involved (see Fig. 1). A square (area = 100 sq. cm.) of dry cellophane (*C*) (Plain Colourless No. 300, obtained from The Cellophane Company Ltd.) was folded over the end of the glass tube *K* (internal diam. = 1 cm.; capacity = 5 c.c.) and bound to it by linen thread (*E*), which was brought to within 1·5 cm. from the end of the tube. In order to prevent rupture of the membrane on application of pressure, it was enclosed in the Pt gauze support B, firmly fixed to *K* by the brass band and bolt *D*. The gauze was of such a size and shape that it supported the whole surface of the distended cellophane. It was essential to weld the strands of the gauze together, for otherwise they became displaced under pressure and afforded insufficient support for the membrane. Before use, the gauze was always thoroughly washed with distilled H_2O and heated in the flame of a Méker burner.

The liquid to be ultrafiltered was placed in *K*, and the latter connected to the pressure apparatus (Fig. 2) by a ground-glass joint, which was held tight by a clamp consisting of brass strips (*R*) drawn together by screw bolts (*M*). Fracture of the glass bearing surfaces was avoided by the insertion of rubber washers (*H*). Connexion was made with the atm. or the pressure apparatus through the three-way tap *O*, which permitted removal of the filter without lowering the pressure in other parts of the apparatus. By means of this system, several filtrations could be carried out simultaneously and independently. All taps were held in position by the spring action of a brass strip (*N*) controlled by screw-clips (*P*).

FIG. 2.



The press. necessary to force liquid through the membrane was produced by means of the apparatus depicted in Fig. 2, which comprised the Hg reservoir *C*, running in an upright rail, the flask *E*, and the glass coil *D*, connected together and with the filters by pressure tubing. Air was drawn into the apparatus by closing the three-way taps, opening taps *A* and *B*, and lowering *C*. On closing *A* and raising *C*, the enclosed air was compressed to about 2 atm. Tap *B* was kept closed during filtration except for a periodical opening to compensate for loss of press. due to decrease in the vol. of the liquid in the filters.

The ultrafiltrates were collected in small glass-stoppered tubes (*A* in Fig. 1). The duration of the filtration was uniformly 4 hrs. Although the filter and receiver were enclosed by a glass tube (*G* in Fig. 1), appreciable evaporation occurred: measurements of the conductivity of pure salt solutions which had been filtered showed a consequent increase in concn. of 6·33%, and this figure was applied as a correction throughout. As there was a possibility of adsorption of acid by the cellophane at the commencement of the filtration, the first two drops of filtrate were always discarded. A series of tests indicated that this was sufficient precaution. All the filtrates were perfectly clear and colourless to the eye.

Determination of the concn. of acid in the filtrates was effected electrometrically by means of the cell

Hg	Hg_2Cl_2, KCl	KCl	Filtrate, Quinhydrone	Pt
	(solid) 3·5M	3·5M	(solid)	foil

The dimensions of the quinhydrone half-cell were such that 0·5 c.c. of filtrate sufficed for a measurement. The cell was set up in an electrically controlled thermostat maintained at 18° (± 0·05°). It was ascertained that the *E.M.F.* reached a steady value in 20 mins. from the immersion of the Pt electrode in the sat. quinhydrone solution. From time to time the reliability of the HgCl electrode was tested by measurement of the *E.M.F.* of a cell similar to the above but with 0·1M-HCl in place of the filtrate. The values observed in no case differed from 0·3872 volt by more than 0·1 mv., which represented the max. error involved in the determination of the null-point.

The method of calculating the actual values of liberated $H^{\cdot}$ is illustrated by an example. The filtrate from a mixture of equal vols. of Sol C and 0·10M-KCl gave an *E.M.F.* of 0·3330 volt; this filtrate was essentially a solution of 0·05M-KCl containing a certain amount of HCl due to the replacement in the S micelles of $H^{\cdot}$ by $K^{\cdot}$, together with a very much smaller amount of polythionic acid, which, for practical purposes, could be regarded as equiv. to HCl. A series of *E.M.F.* determinations with solutions of 0·05M-KCl containing known amounts of HCl showed that the value (y) of the antilogarithm of the expression $-(0{\cdot}450 - E)/0{\cdot}0577$, where E = *E.M.F.*, was directly proportional, over a considerable range, to the concn. (x) of the acid, the mean value of x/y being 1·177.

$x \times 10^3$, millimols./l. ...	12·5	10·0	8·5	7·5	6·0
E.M.F., volt	0·3371	0·3315	0·3272	0·3243	0·3190
$y \times 10^3$	10·64	8·49	7·16	6·37	5·146
x/y	1·175	1·178	1·186	1·177	1·166

Now the value of y corresponding to an *E.M.F.* of 0·3330 volt is $9{\cdot}00 \times 10^{-3}$. It follows that the concn. of acid in the filtrate was $9{\cdot}00 \times 10^{-3} \times 1{\cdot}177 = 10{\cdot}59 \times 10^{-3}M$, and hence, after correction for evaporation, that its concn. in the intermicellar liquid was $10{\cdot}59 \times 10^{-3} \times 0{\cdot}94 = 9{\cdot}95 \times 10^{-3}M$. In a similar manner, the concn. in the absence of salt, *i.e.*, in the intermicellar liquid of a mixture of equal vols. of Sol C and H_2O, was found to be $0{\cdot}43 \times 10^{-3}M$ (Table I). Hence the increase in concn. of acid due to the addition of KCl was $(9{\cdot}95 - 0{\cdot}43) \times 10^{-3} = 9{\cdot}52 \times 10^{-3}M$, or $9{\cdot}52 \times 10^{-6}$ mol. per c.c. Now 100 c.c. of sol and H_2O (or salt) mixture contained $3{\cdot}830/2 = 1{\cdot}915$ g. of S (Table I). The density of the latter being taken as 2, the vol. of S in 100 c.c. of mixture was $1{\cdot}915/2 = 0{\cdot}96$ c.c., and hence the vol. of intermicellar liquid was $100 - 0{\cdot}96 = 99{\cdot}04$ c.c. We have, therefore, that 1·915 g. of S yielded $99{\cdot}04 \times 9{\cdot}52 \times 10^{-6} = 943 \times 10^{-6}$ mol. of acid, *i.e.*, $943/1{\cdot}915 = 492$ micromols. of $H^{\cdot}$ per g. of S were replaced by $K^{\cdot}$. This value is estimated to be correct within ± 3%.

Determination of Adsorption of Total Salt.—The procedure was essentially as follows. Equal vols. of Sol B (Table I) and salt solution were mixed and ultrafiltered, and about 2 c.c. of the filtrate transferred to a porcelain crucible and weighed. The crucible and contents were then heated at 125° for 3 hrs., the dry residue dissolved in a weighed amount of H_2O (about 10 c.c.), and the sp. conductivity of this solution (" conductivity solution ") determined. It was ascertained that no loss of salt resulted from heating under the given conditions. The object of the heating was to eliminate HCl (produced by ionic interchange), and p_H determinations carried out on a number of "conductivity solutions" showed that only traces of acid (of the order $3{\cdot}0 \times 10^{-6}M$) * were present. A correction was made for the very small but measurable conductivity of that portion of the residue which came from the sol itself.

The conductivity measurements were made at 18° ($\pm$ 0·02°) by the ordinary method. A 3 m. bridge was used, and the error in fixing the balance point was about 0·4 mm. The cell constant was determined periodically and showed no change.

The relation between the concn. of the " conductivity solution " and the conductivity was deduced from measurements on solutions containing definite amounts of the particular salt. Having obtained the concn. of the " conductivity solution," the salt content of 1 g. of the filtrate could easily be calculated. The method of calculating the final data is illustrated by the following, the error in the final result being estimated as $\pm$ 10%. 1 G. of the filtrate from a mixture of 2·017 c.c. sol + 2·017 c.c. LiCl aq. contained 46·40 micromols. of LiCl. Hence, correcting for evaporation, 1 g. of intermicellar liquid contained $46{\cdot}4 \times 0{\cdot}94 = 43{\cdot}6$ micromols. LiCl. Now 2·0439 g. of sol and 2·0166 g. of salt solution had been mixed in the first instance, *i.e.*, there were 0·066 g. of S and 3·99 g. of intermicellar liquid present. Therefore the weight of LiCl in the whole of the *intermicellar liquid* was $43{\cdot}6 \times 3{\cdot}99 = 174$ micromols. The concn. of the original salt solution was 0·1014 mol. per 1000 g. solution, so the total amount of LiCl in the whole of the *mixture* was $2{\cdot}0166 \times 0{\cdot}1014/1000 = 204$ micromols. Thus $204 - 174 = 30$ micromols. of $Li^{\cdot}$ had been taken up by 0·066 g. of S, or 455 micromols by 1 g. Determination of the acid content of the filtrate by the method previously described showed that 340 micromols. of $H^{\cdot}$ had been liberated from 1 g. of S; hence 1 g. of S had adsorbed 340 micromols. of $Li^{\cdot}$ by interchange with $H^{\cdot}$, and $455 - 340 = 115$ micromols. of $Li^{\cdot}$ as LiCl, *i.e.*, as total salt.

Observation of Stability.—The sol and salt solution were mixed in a glass-stoppered tube and immediately shaken for 5 mins. Before ultrafiltration, the mixture was kept for a further 5 mins. and its appearance noted; if it was markedly turbid, a second sample was prepared, and examined after standing for 24 hrs. This method of estimating the effect of the salt upon the stability of the sol was sufficiently exact for the immediate purpose. Since the sols were polydisperse, coagulation took place in stages.

Results.

Tables II—IV contain the final results. In all cases the molar concentration of the salt in the sol + salt mixture is shown. The estimated errors in the results are given on p. 2688 and above.

---

* Similar values were obtained for solutions of comparable strength prepared by simple dilution of the stock salt solutions.

TABLE II.

Sol A + sulphates.

Concn. of salt.	Micromols. $H^{\cdot}$ liberated from 1 g. S. Li_2SO_4.	 Na_2SO_4.	 K_2SO_4.
0·005	186	215	260
0·050	535	570	619*
0·500	559	612*	599*

* Denotes complete coagulation.

TABLE III.

Sol C + chlorides.

Salt, and concn.		$H^{\cdot}$ liberated, micromols. per g. of S.	Observations on stability of system.
LiCl	0·005	161	No change.
	0·050	390	,,
	0·150	431	,,
	0·250	482	Very faint turbidity; just perceptible.
	0·500	488	Decided turbidity, followed by settling of small amount S, leaving strong clear sol.
	0·541	482	,, ,, ,, ,, ,,
	1·082	502	Increased turbidity and settling, leaving weak clear sol.
	2·164	537	,, ,, ,, ,, ,,
	4·000	550	Complete coagulation.
KCl	0·005	206	No change.
	0·025	435	,,
	0·0375	497	Very faint turbidity; just perceptible.
	0·050	492	Marked turbidity, followed by settling of small amount S, leaving very turbid supernatant liquid.
	0·075	539	Almost all S settled out, leaving slightly turbid supernatant liquid.
	0·100	531	Complete coagulation. Whole of S settled out rapidly.
	0·250	546	,, ,, ,, ,, ,,
	0·500	546	,, ,, ,, ,, ,,
	1·750	550	,, ,, ,, ,, ,,
$MgCl_2$	0·005	—	No change.
	0·0125	—	Very turbid. Trace settling.
	0·0187	—	Bulk of S settled out, leaving weak clear sol.
	0·0200	—	,, ,, ,, ,, ,,
	0·0225	—	Complete coagulation.
	0·0250	542	,, ,,
	0·050	550	,, ,,
	0·500	555	,, ,,

TABLE IV.

Sol B + 0·05M-chlorides.

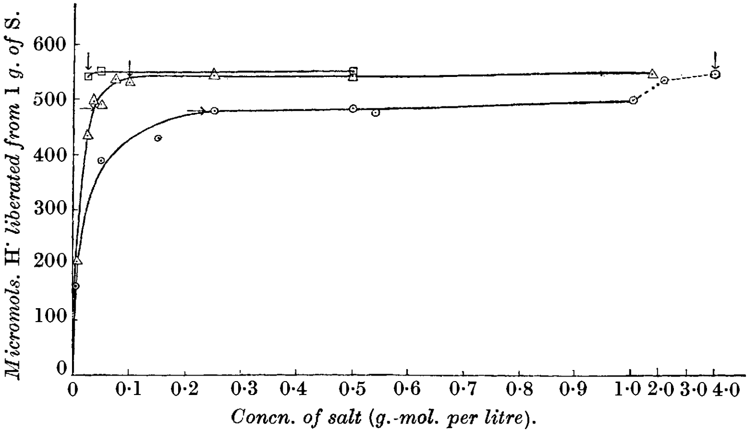
Salt.	Micromols. of kation adsorbed per g. of S. By exchange with $H^{\cdot}$.	 As total salt.
LiCl	337	117
NaCl	364	171
KCl	407	248

DISCUSSION.

Ion Exchange.—The data presented in the foregoing tables and in Fig. 3 show conclusively that, of the alkali kations studied, potassium has the greatest tendency to replace hydrion in the sulphur micelles, and lithium the least. The following interpretation of this occurrence of the lyotropic sequence is developed from the point of view suggested by Achar and Usher (J., 1927, 1875) (cf. Freundlich, "Kapillarchemie," 1932, 195; McBain, *J. Physical Chem.*, 1924, **28**, 706, Pauli and Valkó, "Elektrochemie der Kolloide," Wien, 1929, 103; Usher, *Trans. Faraday Soc.*, 1925–1926, **21**, 406; Wilson, *J. Amer. Chem. Soc.*, 1916, **38**, 1982). The polythionic acid in the micelles undergoes dissociation to give hydrogen ions which diffuse but whose range of movement is limited, being determined by the electrostatic field of the anions, which are attached to the surface of the sulphur. Hence, the sulphur particle and its adsorbed acid may be conceived as separated from the bulk of the intermicellar liquid ("external liquid") by an imaginary envelope which marks the limiting range of movement of the hydrogen ions and is equivalent to a membrane permeable to all ions with the exception of the polythionate ions held by the sulphur. If, now, a neutral salt is introduced into the external liquid, exchange will take place between some of the hydrogen ions within the envelope and an electrically equivalent amount of metal ions from the external liquid. A state of equilibrium of the Donnan type will be finally attained.

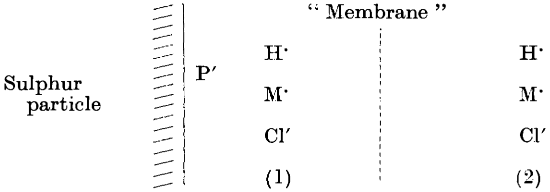
FIG. 3.

Sol B + chlorides (Table III).



-⊙- Li ; -△- K ; -⊡- Mg ; ⟶ = *commencement of coagulation* ; ↓ = *complete coagulation.*

In order to account for the differences in amount of exchange shown by the various kations under the same conditions, it is suggested that the metal polythionates possess different degrees of "surface dissociation." We may examine the effect of the formation of un-ionised polythionate on the equilibrium distribution of the ions by means of the following representation, in which, for simplicity, the polythionic acid is taken as completely ionised.



P′ — polythionate ion "bound" by sulphur. The small amount of "free" polythionate is neglected. $M^{\cdot}$ — kation of added neutral salt (chloride).

According to the Donnan principle, the distribution at equilibrium of hydrogen ion between (1) and (2) depends upon the relation between the concentration of salt in (2) and of polythionate ion in (1): the smaller the concentration of P′ compared with that of MCl, the more equal is the distribution (Donnan, *Z. Elektrochem.*, 1911, **17**, 572). Hence, combination of $M^{\cdot}$ with P′ to form un-ionised polythionate will tend to equalise the concentrations of hydrogen ion in (1) and (2), *i.e.*, to promote interchange of $M^{\cdot}$ with $H^{\cdot}$. Thus the tendency of a kation to replace $H^{\cdot}$ will be the greater, the smaller the degree of surface dissociation of the corresponding polythionate. It follows that the degrees of surface dissociation of the alkali-metal polythionates have the order Li $>$ Na $>$ K.

Mechanism of Coagulation.—The curve for potassium chloride in Fig. 3 becomes horizontal at a salt concentration of 0·1*M*; this is therefore the concentration at which the salt is just able to liberate the whole of the hydrogen ion from the micelles. The observations on the stability of the sol (Table III) show that this is the concentration required just completely to coagulate the sol. Similarly, with lithium chloride (and, in all probability, with magnesium chloride also), complete coagulation coincides with maximum replacement of hydrogen ion. Further, those concentrations of lithium and potassium chloride which produce the first sign of coagulation (*i.e.*, of the coarsest particles) liberate the same amount of hydrogen ion. It thus appears highly probable that the micelles of any given size aggregate always and only when the concentration of added salt is such that ionic interchange is complete. The data in Table II, though less decisive since they do not comprise "threshold" values, are obviously also in accord with this conclusion.

By applying the above theory, it follows that the condition for coagulation is the complete suppression of the ionisation of the polythionate in the micelles, since in the postulated Donnan equilibrium the distribution of the hydrogen ion between the surface layer and the external liquid can become uniform only if the concentration of polythionate ion is reduced to zero.

Bassett and Durrant (*loc. cit.*), working with sols stabilised by sodium polythionate, found that the coagulum invariably contained the positive ion of the coagulant in amount equivalent to the bound polythionate. This result is supported by the present work, which, however, goes a step further by showing that coagulation takes place *as soon as* the ionic interchange is complete. Bassett and Durrant regard the coagulation process as very similar to the precipitation of ordinary insoluble salts. This view has common ground with the one proposed here, since both imply that the coagulation is preceded by complete neutralisation of the charge on the colloidal particles.

Adsorption of Anions.—Bassett and Durrant (*loc. cit.*) could not detect any trace of the anion of the coagulating salt in the sulphur coagulum. Odén (*loc. cit.*), however, reports that sodium chloride, and Rindé (*loc. cit.*) that hydrogen chloride, is adsorbed by the sulphur. The experiments carried out on sol B (Table IV) show conclusively that anion adsorption (adsorption of total salt) occurred in our sols. The sols studied by Bassett and Durrant were undialysed, which may explain the difference in behaviour.

The adsorption of chloride gives the lyotropic series also, for we have K $>$ Na $>$ Li. Assuming that chloride ions are actually fixed to the sulphur surface, the number attached will depend, *ceteris paribus*, upon the concentration of chloride ions in the neighbourhood of the surface. This, in turn, will be determined by the " membrane " equilibrium envisaged earlier in the discussion. Owing to the presence of non-diffusible polythionate ions, the equilibrium concentration of chloride ion in (1) will be less than in (2), and, as previously pointed out, the inequality in the distribution will be greater the higher the concentration of non-diffusible ion. Since potassium forms the least ionised polythionate, it follows that the concentration of chloride ion in the surface layer of solution, and hence the amount bound by the sulphur, will be greatest in the case of potassium chloride.

With highly concentrated sols, the adsorption of the anion of the added salt probably complicates the study of the cationic interchange. If, for example, a chloride is added in sufficient quantity, a high concentration of hydrogen chloride will be produced, and the possibility arises that some hydrogen ion may be adsorbed in this form after all the polythionic acid has been converted into un-ionised salt. In these circumstances, complete coagulation would take place before the whole of the hydrogen ion appeared in the intermicellar liquid. This behaviour was indicated by the results of some preliminary experiments on a portion of sol C which had been concentrated to about four times the original strength by evaporation at 50°. It was found that, while the total available hydrogen ion was 530 micromols. per g. of sulphur, complete coagulation was produced by 0·075M-magnesium chloride, at which concentration the liberated hydrogen ion amounted to only 450 micromols. An observation recorded by Odén (*loc. cit.*, p. 134) is of interest in this connexion. He found that the coagulum produced by the action of sodium chloride upon a sol stabilised by sodium polythionate, and to which hydrochloric acid (0·407M) had been added, was decidedly more acid than the supernatant liquid. Moreover, the amount of sodium in the coagulum was less than when coagulation was brought about in the absence of hydrogen chloride, although a very much smaller concentration of sodium chloride sufficed in the latter case. It seems certain that in the presence of hydrogen chloride the coagulum carried down a considerable quantity of the acid, adsorbed on the sulphur.

SUMMARY.

1. Measurements of the adsorption of the ions of alkali-metal salts by the micelles in sulphur sols stabilised by a polythionic acid show that the lyotropic series occurs in the ionic interchange and also in the adsorption of total salt.

2. The ionic interchange can be correlated with coagulative action, since it appears that, provided the concentration of acid in the system be not too high, coagulation takes place at that concentration of salt which just suffices to liberate the whole of the hydrogen ion.

3. A reasonable interpretation of the results obtained is given in terms of the Donnan equilibrium and the theory of surface dissociation.

The authors' thanks are due to Imperial Chemical Industries Ltd. and to the Earl of Moray Endowment for assistance in the purchase of apparatus.

THE UNIVERSITY, EDINBURGH. [*Received, September 6th,* 1932.]