66. *Ionic Interchange in Sulphur Sols. Part IV. The Action of Multivalent Metallic Ions.*

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The interchange between salt kations and hydrogen ions pertaining to the polythionic acid present in the micelles of sulphur sols has been investigated in the case of lithium chloride, barium chloride, and neodymium nitrate. It is found that the amount of replaced hydrogen ion is the same for all three salts at the respective " threshold " coagulating concentrations. This result is in harmony with the view that the degree of interchange at the coagulation point is independent of the nature of the coagulating kation. The relation of the interchange to the coagulation process is discussed.

THE liberation of hydrogen ions from the micelles in sulphur sols by interchange with the kations of added salts has been investigated by Weiser and Gray (*J. Physical Chem.*, 1935, **39**, 1163), who conclude that, in contrast to the behaviour of the alkaline-earth kations, thorium, neodymium, and aluminium completely coagulate the sol before the maximum displacement of hydrogen ion is attained. According, however, to the data of Bolam and Muir (J., 1933, 1022), aluminium displaces the same fraction of hydrogen ion as the alkali and alkaline-earth kations, under comparable conditions. Evidence has now been obtained that neodymium also is not exceptional.

EXPERIMENTAL.

Coagulation.—Colloidal (Raffó) sulphur was prepared as described by Bolam and Bowden (J., 1932, 2684), except that the sol was not dialysed. In one series of experiments, designed to ascertain the " threshold " coagulation values of the salts, equal volumes (2 ml.) of sol and salt solution were brought to 0°, mixed, and the coagulation of the sulphur examined either immediately, or after the mixture had been kept at 0° for some time. Similar experiments were also carried out at room temperature (about 18°). A Zeiss nephelometer and a Pulfrich photometer were used to investigate the coagulation by measurement of the intensity of the light scattered by the sulphur in the mixture. For such measurement a portion of the mixture was placed in a 2·5-mm. deep, plane-sided, glass cell. The direct beam was passed through the ground-glass screen No. 4, and compared with the Tyndall beam after both had passed through the green filter L_2. The data are given in Table I, where each nephelometric value (*i.e.*, value of the so-called " relative opacity ") represents a quite independent determination in the great majority of cases. As elsewhere, salt concentrations are expressed as milliequivs. of kation in 1 l. of the mixture of sol and salt solution.

TABLE I.

Temperature = 0°.

Salt.	Concn.	0 hr.	½ hr.	1 hr.	2 hrs.	Salt.	Concn.	0 hr.	½ hr.	1 hr.	2 hrs.
—	—	504	—	—	—	Nd(NO₃)₃	0·475	—	505	505	—
LiCl	50	—	505	—	—		0·500	505	—	—	505
	150	—	505	505	—			513			
	200	—	551	553	—			512			
			553				0·532	544	544	—	—
	250	—	592	—	—		0·549	—	572	—	—
BaCl₂	0·500	—	—	—	505		0·588	—	621	—	—
	0·667	505	—	—	506		0·667	719	—	—	719
		508						730			
	0·678	541	549	548	—						

Temperature = *ca.* 18°.

Salt.	Concn.	0 hr.	½ hr.	1 hr.	2 hrs.	Salt.	Concn.	0 hr.	½ hr.	1 hr.	2 hrs.
		549				—	—		500	—	—
	0·682	588	—	—	—				505		
	0·690	610	—	—	—				505		
		617							505		
	0·698	667	—	—	—				505		
	0·714	676	—	—	680	BaCl₂	0·714	505	—	505	—
	0·769	826	—	—	826		0·769	548	—	548	—
						Nd(NO₃)₃	0·714	694	694	—	—
							0·769	1811	1811	1811	1811

In another series of experiments, covering almost the whole range of coagulation, equal volumes (2 ml.) of sol and salt solution were mixed at room temperature, coagulated sulphur removed by filtration through a sintered-glass filter of the finest porosity (5/3), and the nephelometric value of the (uncoagulated) sulphur in the filtrate determined.   Table II gives the data obtained.

TABLE II.

Temperature = *ca.* 18°.

Salt concn.	—	0.500	0.667	0.833	0.909	1.000	1.053	1.111	1.250	1.667	2.50
Nephelometric value { BaCl₂	505	508	508	464	362	145	54	33.9	24.5	17.2	9.0
{ Nd(NO₃)₃	—	505*	504	(317)	244	84.7	19.6	15.3	9.8	9.6	9.2

* Unfiltered.

Ionic Interchange.—Equal volumes (2 ml.) of sol and salt solution were mixed, and the mixture ultrafiltered at 0° by means of the apparatus described by Bolam and Bowden (*loc. cit.*). The bulk of the acid in 2 ml. of ultrafiltrate was neutralised by the addition of a known volume of 0·00627N-sodium hydroxide, and the remainder estimated by means of the quinhydrone electrode, the measurements being carried out in an air-thermostat maintained at 25·0° $\pm$ 0·2°. Determinations with mixtures of hydrochloric acid and sodium hydroxide of known composition showed that the concentration (in equivs./l.) of un-neutralised acid (c) was given, in general, to within 3%, by the formula $E.M.F.$ (millivolts) = 446·1 + 59·1 log c. It was found that the presence of the salts, at the concentrations employed, was without influence on the $E.M.F.$

Table III contains the data for the sulphur sol, the total concentration (in milliequivs./l.) of acid in the ultrafiltrate being given by the expression $1000[(2 + x)c + 0·00627x]/2$, where

TABLE III.

Temperature = 0°.

Salt.	Concn.	x (ml.).	$E.M.F.$	$c \times 10^3$	Total acid in ultrafiltrate (m.-e./l.).	Replacement value (m.-e./l.).	Degree of interchange.
—	—	4.002	259.9	0.706	14.664	—	0.00
			260.0	0.710	14.676		
		4.464	233.5	0.254	14.816		
			233.0	0.248	14.797		
LiCl	150.0	4.464	242.8	0.363	15.168	0.430	0.49
			244.0	0.380	15.224	0.486	
		4.649	180.6	0.032	14.682 *	0.453	
			179.0	0.030	14.675 *	0.446	
	200.0	4.464	243.5	0.372	15.197	0.459	0.52
			243.9	0.378	15.217	0.479	
		4.649	192.3	0.051	14.744 *	0.515	
			189.6	0.046	14.727 *	0.498	
BaCl₂	0.667	4.464	242.2	0.356	15.146	(0.408)	0.55
		4.649	228.3	0.206	15.260	0.522	
			227.8	0.202	15.247	0.509	
	0.678	4.464	244.8	0.393	15.265	0.527	0.55
			244.4	0.386	15.243	0.505	
Nd(NO₃)₃	0.475	4.649	224.9	0.181	15.177	0.439	0.48
			225.7	0.187	15.197	0.459	
	0.532	4.464	243.9	0.378	15.217	0.479	0.53
			244.3	0.385	15.240	0.502	
	10.0	4.464	242.8	0.363	15.168 *	0.939	1.00
			244.1	0.382	15.230 *	1.001	
		4.649	238.4	0.306	15.592	0.854	

x is the volume of alkali added. The " replacement value " is the amount of hydrogen ion liberated by ionic interchange, and is equal to the difference between the total acid in the ultrafiltrate from sol + water (mean value = 14·738 milliequivs./l.), and that from sol + salt. Some of the determinations (marked with an asterisk) were carried out after filtering the sol through an ordinary filter-paper, to remove coarse sulphur. As will be seen, a quantity of intermicellar acid was also removed, and the replacement values in these instances are deduced on the assumption that the total acid in the ultrafiltrate from sol + water was 14·229 milliequivs./l. Since the interchange was undoubtedly complete in the case of 10·0 milliequivs./l. neodymium nitrate, the degree of interchange is obtained by dividing the mean replacement value by 0·931.

In certain cases, nephelometric and replacement values were determined in the early stages of the work and redetermined near its conclusion, and the agreement obtained shows that no appreciable change occurred in the sol during the interval.

Apparatus and Materials.—With the exception of the burette used for the addition of alkali, Pyrex or Jena-glass apparatus was employed throughout. The lithium chloride solution was prepared from twice recrystallised B.D.H. anhydrous salt, and standardised with silver nitrate. Good crystals of neodymium nitrate hexahydrate were obtained from B.D.H., and used without further purification. All other chemicals were of A.R. or " AnalaR " quality.

DISCUSSION.

In the case of the experiments in Table I, coagulation was accompanied by an increase in the nephelometric value, and could be detected in this way even when no change was apparent to the unaided eye. It will be seen that at all concentrations of the salts the nephelometric value did not vary with time, from which it follows that any aggregation of the particles was rapid and gave rise to a stable suspension. As is well known, sulphur sols undergo fractional coagulation (Odén, *Nova Acta Upsala*, 1913, iv, **3**, 156), the larger particles being coagulated by salt concentrations lower than those necessary to produce aggregation of the smaller particles. The present data therefore indicate that the coagulation of each fraction is a rapid process, becoming complete shortly after the addition of the coagulant.

It is not possible to obtain comparable coagulation values by determining the concentrations which produce any given increase in the nephelometric value, since this does not bear the same relation to the extent of coagulation in all cases. If the nephelometric values are plotted against salt concentrations, it is found that an approximately straight line is obtained in the region of coagulation, but that the slope of the neodymium nitrate line is definitely less than that for barium chloride. Assuming that any given nephelometric value uniformly represented the same degree of coagulation, it would follow that an increment in the concentration of barium chloride produced a greater amount of coagulation than the same increment in the case of neodymium nitrate. This, however, cannot be the fact, since the neodymium salt is clearly the more powerful coagulant (see Table II). It is evident that the nature of the aggregates varies from salt to salt, which would be anticipated from observations on the properties of sulphur coagula (Odén, *loc. cit.*; Weiser and Cunningham, " Colloid Symposium Monograph," 1928, **6**, 319; Bassett and Durrant, J., 1931, 2919). For all practical purposes, however, the sol may be said to possess the same degree of instability at the respective " threshold values " of the salts, *i.e.*, the concentrations which produce the first trace of coagulation, and hence just suffice to raise the nephelometric value above that for sol + water (= 505). Under these conditions any error due to differences in the state of aggregation will be negligibly small.

TABLE IV.

Temperature = 0°.

Salt.	Threshold value.	Replacement value.	Degree of interchange.
LiCl$_2$	150·0	0·453	0·49
BaCl$_2$	0·673	0·516	0·55
Nd(NO$_3$)$_3$	0·500	0·470	0·50

Table IV contains the threshold values obtained at 0°. The value given for lithium chloride may be somewhat low, but cannot be as great as 200 milliequivs./l., and that for the neodymium salt may be very slightly high. The corresponding data for the liberation of hydrogen ion are also given in Table IV, the figures for neodymium nitrate being deduced from the experimental data in Table III on the assumption that the replacement is directly proportional to the salt concentration. Justification for this assumption lies partly in that a very limited concentration range is involved, and also in that, at the degree of interchange in question, such proportionality has been observed in other cases.

It will be seen that divergence from the mean value of 0·51 for the degree of interchange amounts to − 4% in the case of lithium, + 8% in that of barium, and − 2% in that of

neodymium. These variations must to a large extent be due to experimental error, and may be wholly so, since previous work (Bolam and Muir, *loc. cit.*; J., 1934, 754) indicates that lithium and barium produce the same amount of replacement under comparable conditions. No appreciable effect due to difference in the nature of the salt anion is to be expected. Odén (*loc. cit.*) found that the coagulation values of the nitrates of potassium, calcium, and barium were practically identical with those of the respective chlorides, and Freundlich and Scholz (*Kolloid-Chem. Beih.*, 1922, **16**, 234) showed that the coagulation value of barium chloride was very close to that of the nitrate. Bolam and Muir (*loc. cit.*) have also observed that the relation between interchange and coagulating action is the same for potassium chloride, potassium sulphate, ammonium chloride, and ammonium iodide, although the coagulation values differ considerably.

The present data thus indicate that lithium, barium, and neodymium produce the same degree of interchange when present in concentrations which just suffice to coagulate the coarsest particles. According to Bolam and Muir (J., 1933, 1022), equivalence in interchange is shown by potassium, rubidium, calcium, and aluminium, when compared at the point of complete coagulation, *i.e.*, at the minimum concentrations required to coagulate the finest particles. These results support the view that, for any one sol, the amount of interchange which accompanies a given degree of coagulation is constant, being independent of the nature of the coagulating kation. On the other hand, Weiser and Gray (*loc. cit.*) maintain that, under comparable conditions, the interchange is exceptionally low in the case of multivalent metallic ions. Weiser and Gray studied the interchange in a well-dialysed Raffó sol, and the replacement values given by them yield the following values for the degree of interchange at the point of complete coagulation : Ba = 1·0, Sr = 1·0, Nd = 0·65, Al = 0·69, Th = 0·58.

It is difficult to give a satisfactory explanation of the lack of agreement. To some extent it may be due to the manner in which Weiser and Gray deduce their replacement values, since they ignore interchange of salt kations with those hydrogen " counter " ions which can be detected potentiometrically in the pure sol. If allowance be made for such ions, and Weiser and Gray's estimate of their amount accepted, the degree of interchange for neodymium would be about 0·81 (instead of 0·65). The actual figure, however, is probably somewhat less than this, since Weiser and Gray assume that all the potentiometrically active hydrogen ions in the pure sol are situated in the outer part of the electrical double layer of the particles, whereas it is almost certain that an appreciable proportion of them are due to the presence of unadsorbed polythionic acid in the bulk of the intermicellar liquid. It may also be pointed out that there are certain apparent inconsistencies in the results of Weiser and Gray. According to their *direct* determinations of the amounts of salt kation taken up by the sulphur particles at the coagulation point, neodymium and barium were adsorbed to practically the same extent (0·68 : 0·71) in the case of one sol, whereas in that of another, the adsorption of neodymium was much less than that of barium (0·52 : 0·74). Further, their data appear to indicate that in the case of a Selmi sol, neodymium shows greater replacing power than barium, but that the reverse holds in the case of a Raffó sol, at least up to the point of complete coagulation by neodymium. In view of the very similar constitution of the two sols, this state of affairs is improbable.

Verwey and Kruyt (*Chem. Reviews*, 1935, **16**, 407; " Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions," 1937, reprinted from *Chem. Weekblad*, 1938, **35**, 77) are of the opinion that, in general, the interchange plays no significant part in the coagulation process. This view is considered to receive strong support from certain experiments (*Z. physikal. Chem.*, 1934, *A*, **167**, 312) which are regarded as showing that, in some cases, the concentration of salt required to produce complete coagulation of colloidal silver iodide, stabilised by hydriodic acid, is much greater than that necessary to effect complete replacement of the hydrogen ions. Two recent investigations, however, suggest that Verwey and Kruyt's interpretation of their data should be regarded with considerable reserve. In the first place, Weiser, Milligan, and Coppoc (*J. Physical Chem.*, 1938, **42**, 427) have shown that silver iodide sol undergoes fractional coagulation, so that the small proportion of very fine particles present requires a much higher salt concentration for coagulation than does the great bulk of the colloid. Hence, since only a relatively

very small amount of hydrogen ion will remain unreplaced when the bulk of the sol has been coagulated, the interchange might *appear* to be complete, although not actually so, at a concentration much lower than that needed to coagulate the finest particles, *i.e.*, to produce complete coagulation.   In the second place, de Bruyn and Overbeek (*Kolloid-Z.*, 1938, **84**, 186) have shown that in sols prepared by the method of Verwey and Kruyt, the replaceable ions are not exclusively hydrogen ions.   In the sols actually examined, ions other than hydrogen accounted for one-quarter to two-thirds of the total amount of counter-ions.   It follows that the replacement of hydrogen ion in such sols may be practically complete at a concentration of the coagulant much lower than that required to complete the interchange as a whole, which is the factor in question.

In agreement with the results of previous work, the present investigation shows that in sulphur sols the degree of interchange is the same at concentrations of the various salts which produce the same degree of instability, although the *equilibrium* concentrations of the salt kations may differ very widely.   As may be deduced from Table IV, while the degree of interchange is constant to within a few units %, the equilibrium concentration of the lithium ion (*i.e.*, the concentration in the intermicellar liquid after interchange had taken place) is about 1000 times that of the barium ion, and about 5000 times that of the neodymium ion.   It is therefore difficult to avoid the conclusion that in these sulphur sols the interchange exercises a predominating influence on the coagulation.   The simplest explanation of this state of affairs is that the salt kations form some kind of neutral complex with the adsorbed polythionate anions, so that the surfaces of the particles are discharged to the same extent by salt concentrations producing the same degree of interchange.   Presumably the forces involved in the formation of the surface complexes are those responsible for the " adherence " or " attachment " of counter-ions to the micelles of paraffin-chain salts (Hartley, " Aqueous Solutions of Paraffin-Chain Salts," 1936, 32 ; *Trans. Faraday Soc.*, 1938, **34**, 1284).

In certain instances, *e.g.*, the mineral-oil emulsions studied by Powis (*Z. physikal. Chem.*, 1915, **89**, 186) and Limburg (*Rec. Trav. chim.*, 1926, **45**, 772), there is no evidence of even the existence of ionic interchange.   It therefore appears necessary to distinguish between stabilisation due to the adsorption of specific ions, and stabilisation due to some other non-specific process (cf. Kruyt, *Trans. Faraday Soc.*, 1935, **31**, 31 ; Verwey, " Colloid Symposium Monograph," *loc. cit.*, p. 67 ; Usher, *Kolloid-Z.*, 1935, **71**, 177).   Although the second of these factors is solely responsible for the stability of the oil emulsions, both will be operative in the case of colloidal sulphur.   Hence, a reasonable interpretation of the behaviour of sulphur sols is that nullification of the stabilising influence of the adsorbed polythionate ions depends upon the attainment of a certain degree of interchange, which always requires a concentration of salt greater than that necessary to eliminate the other stabilising factor.   Moreover, on the assumption that Kruyt and Verwey's data for silver iodide sols *are* substantially correct, these systems may possibly be regarded as an intermediate case, the stabilising influence of the adsorbed iodide ions being removed by concentrations of salts lower than those required to bring about actual coagulation.   The interchange would thus play an essential, though minor, rôle in the coagulation process.   It is to be expected that, in general, the coagulation value will be the more obviously related to the degree of interchange, the greater the surface density of the adsorbed stabilising ions.

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